KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM

PROCEEDINGS

VOLUME XXVIII

N°. 7

President: Prof. F. A. F. C. WENT

Secretary: Prof. L. BOLK

(Translated from: "Verslag van de gewone vergaderingen der Afdeeling Natuurkunde", Vol. XXXIV)

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Chemistry. — *"On a Qualitative Resemblance between the Velocity of Hydration of Acid Anhydrides and the Velocity of Hydrolysis of Diacylperoxides"*. By Prof. J. BÖESEKEN and H. GELISSEN.

(Communicated at the meeting of May 30, 1925).

BRODIE [1]), the discoverer of the organic peroxides, or more in particular of the acylperoxides (which are derivatives of H_2O_2 in which one or both H atoms have been replaced by an acyl rest) already found that they are decomposed by water into free acid and oxygen.

A considerable time later V. PECHMANN and VANINO [2]) observed that phtalylperoxide was comparatively rapidly changed into phtalic acid and hydrogen peroxide by alkalies and their carbonates.

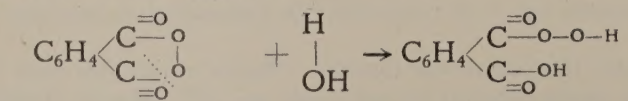
Neither BRODIE nor V. PECHMANN and VANINO entered any further into the mechanism of this decomposition.

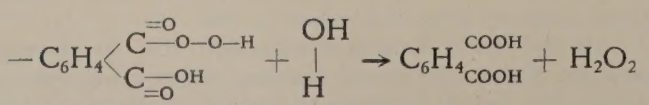
VON BAEYER and VILLIGER [3]) found that phtalylperoxide, on careful treatment with alkali-hydroxides in the cold, first changes into the alkali-salt of phtalylmonoperacid. These investigators also observed that the two-sided substituted H_2O_2-derivatives by no means act rapidly oxidizing, but only become active when they have been converted into the one-sided substituted derivatives by hydrolysis [4]).

The difference in velocity of hydrolysis between acetylbenzoyl-, diacetyl-, and dibenzoyl-peroxide observed by these investigators, was no further accounted for by them.

From the fact that VON BAEYER observed the formation of hydrogen peroxide when the phtatylperoxide was heated with alkali-hydroxide, in connection with what precedes, follows the course of the reaction between diacylperoxides and water.

The reactions that take place when H_2O acts on phtalylperoxide, are n our opinion the following:





$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

[1]) An. 1863. III Supl. 211.

[2]) Ber. 27, 1511, 1894.

[3]) Ber. 34, 765, 1901.

[4]) The action of dibenzoyl- and acetylbenzoyl-peroxide on a solution of indigo-blue (disulphonic acid-indigo dissolved in H_2O is discoloured with formation of isatine) or on a KI solution is ascribed by V. BAEYER (Ber. 33, 1569, 1900) to the action of the per-acid formed intermediarily.

(Remark. The structure formula of the phtalylperoxide given here, was proved by us (see Chem. Weekblad 22, 187, 1925); we also point out at once that the splitting up takes place in the bond C—O and not in the bond O—O—).

VON BAEYER [1]) succeeded in converting benzoylperoxide, which can resist cold alkali, into benzoyl hydroperacid-Na and benzoic acid ethylester through careful saponification with sodium ethylate.

The reaction:

$$C_6H_5COOOCO\,C_6H_5 + C_2H_5O\,Na \rightarrow C_6H_5C^{=O} - O - O\,Na + C_2H_5\,COO\,C_6H_5$$

shows that on hydrolysis of the diacyl peroxides *not* the —O—O-bond is broken, but the $-C^{=O}_{-O}$ bond, since in C_2H_5ONa not the — ONa group combines with a C_6H_5COO-part, but the Na combines with the C_6H_5COOO-part of the benzoyl peroxide-molecule, as one of us will show more in detail.

Through an *aqueous* alkali-solution VON BAEYER could change diacetyl peroxide into aceto peracid and acetic acid.

We shall see presently that the difference between benzoyl peroxide and acetyl peroxide towards aqueous alkalies consists simply in a difference in velocity of hydrolysis.

FREER and NOVY [2]), who examined the oxidizing action and the behaviour towards certain bacteria of benzoyl acetyl- and of diacetyl peroxide, agreed with VON BAEYER that benzoylacetyl peroxide as such is no direct oxidizing substance.

They write: "Pure benzoylacetyl peroxid is not an oxidising substance, nor has it any odor, a fact which was also observed by BAEYER".

These investigators found further that on hydrolysis of benzoylacetyl peroxide in aqueous solution a precipitate of dibenzoylperoxide is formed, which they represent by the following equation:

$$C_6H_5C^{=O}OOC^{=O}CH_3 + C_6H_5COOH \rightarrow C_6H_5COOOCOC_6H_5 + CH_3COOH,$$

(in other words the primary product of hydrolysis C_6H_5COOH of the benzoyl acetylperoxide acts on unchanged benzoylacetyl peroxide).

Also these investigators observed the insensibility of dibenzoylperoxide to water; for they write: "On the other hand, benzoylperoxid is difficultly soluble, does not undergo hydrolysis, has no oxidising action, and is wholly without effect upon bacteria".

Accordingly FREER and NOVY have entered again somewhat more deeply into the process of hydrolysis of the diacylperoxides, and on the ground of this they could furnish the proof that symmetrical acylperoxi-

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[1]) Ber. 33, 1569, 1900.

[2]) Am. 27, 161, 1901.

des are inert towards definite bacteria, whereas the peracids are strong poisons to these same bacteria.

The hydrolysis of the diacylperoxides has been most successfully studied by CLOVER and RICHMOND [1]).

These investigators came to the following conclusions:

1. Diacylperoxides are completely hydrolysed into acid and peracid by water.

The duration of the reaction is dependent on the solubility in water and on the nature of the peroxide.

The reaction:

$$ROOR + H_2O \rightarrow ROH + ROOH \qquad (R = \text{acylrest})$$

is *not* reversible according to these investigators, and proceeds therefore quantitatively in the direction towards the right.

In mixed peroxides the hydrolysis goes in two directions:

$$ROOR_1 + H_2O \rightarrow ROH + R_1OOH,$$

or

$$ROOR_1 + H_2O \rightarrow ROOH + R_1OH.$$

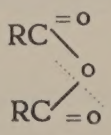
2. Peracids hydrolyse into acid and hydrogen peroxide.

According to CLOVER and RICHMOND this reaction is *not* reversible either; it proceeds more slowly than the hydrolysis of the diacylperoxides and is accelerated by acids.

They found that a 5 % solution of diacylperoxide was completely hydrolysed according to equation 1 in 24 hours, that buteric acid peroxide, and also crotonic acid peroxide, hydrolysed much more slowly, and that "with benzoic peroxide it is so slow as to be scarcely detected in the course of several days".

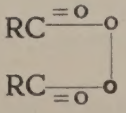
We shall discuss this difference in velocity of hydrolysis of these diacylperoxides more in detail later on, and only state now that C. and R. do not enter any further into this matter.

When we compare the reaction of hydration of the acid anhydrides [2])



$$+ H_2O \rightarrow RCOOH + RCOOH \qquad (I)$$

and the reaction of hydrolysis of the diacylperoxides,



$$+ H_2O \rightarrow RCOOOH + RCOOH \qquad (II)$$

we observe:

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[1]) Am. 29, 180, 1903.

[2]) According to VERKADE (Diss. Delft) the two successive reactions for fatty acidanhydrides are; Anhydride + H_2O → addition product; addition product → 2 mol. acid.

1. that in both cases a C—O-bond is broken up through the action of the water,

2. that the reaction products are two acids in both cases,

3. that both I and II are accelerated through alkali hydroxides, carbonates, and bicarbonates, as was found by ORTON and JONES [1]) for the hydration of acid anhydrides, and by VON BAEYER (loc. cit.) for the hydrolysis of the diacylperoxides.

4. that both reactions are catalytically affected by acids, which was observed by CLOVER and RICHMOND (loc. cit. p. 184) for the diacylperoxides, and by ORTON and JONES (loc. cit. and Dissertatie VERKADE p. 17) for the hydration of the anhydrides.

These facts have led us:

I to consider the diacylperoxides as anhydrides of peracids and acids;

II to draw up the rule:

Diacylperoxides derived from acid anhydrides which have a small hydration constant, do not hydrolyse, or they hydrolyse exceedingly slowly.

This rule, which expresses a qualitative relation between the velocity of hydration of the acid anhydrides, and the velocity of hydrolysis of the diacylperoxides, enables us therefore to derive the properties of the diacylperoxide from those of the corresponding anhydride, in which it appears that the velocity of hydrolysis of the diacylperoxide is always smaller than that of the corresponding anhydride, which follows from a comparison of the reaction constants in question.

VERKADE (Diss. Delft, p. 56) found that the hydration reaction of the lower acid anhydrides (up to C_5) satisfies the equation of a mono-molecular reaction (excess of H_2O), and CLOVER and RICHMOND observed that the hydrolysis of the diacylperoxides likewise takes place according to the equation:

$$K = \frac{1}{t} \log. \frac{a}{a-x}$$ hence also as a reaction of the first order.

VERKADE observed that the velocity of hydration of the anhydrides of acetic acid, propionic acid, and butyzic acid decreased from the left towards the right; it may be concluded from CLOVER and RICHMOND's investigations that the velocity of hydration of the peroxides of acetic acid, propionic acid, and butyzic acid likewise greatly decreases from the left towards the right.

CLOVER and RICHMOND found two peroxides that do not hydrolyse at all, viz. crotonic acid peroxide and benzoylperoxide. About crotonic acidperoxide they say (loc. cit. p. 196). "The slowness with which it hydrolyses, however, renders it suitable for such study", and about benzoylperoxide "with benzoic peroxide it (i.e. the hydrolysis) is so slow as to be scarcely detected in the course of several days".

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[1]) J. Chem. Soc. **101**, 1708, 1917.

Striking is the agreement in the behaviour of the corresponding acid anhydrides in question towards water resp. towards hydrolysing agents.

Of benzoic acid anhydride we find stated (V. MEYER and JACOBSON II 547). "Es ist sehr beständig gegen Wasser und wässerige Natronlauge", while VANINO (Handbuch II, 612) says that it "selbst gegen heisse Sodalösung mäszig beständig ist", and it moreover follows from CLOVER and RICHMOND's researches that crotonic acid anhydride is *not* converted to crotonic acid by soda solution (p. 194 loc. cit.). We see from this that this agreement in velocity of hydration of the two anhydrides that are insensible to water corresponds to the velocity of hydrolysis of the peroxides that are likewise insensible to water: both velocities are very small. As was stated above, the velocity of hydrolysis of the diacylperoxides is smaller than the velocity of hydration of the anhydrides.

In order to show this agreement in velocity of hydration further we have made a few new diacyl peroxides, derived from acids whose anhydrides are insensible to water. These peroxides appeared likewise insensible to the action of water.

They are:

Cinnamoylperoxide. Melting point 144° C. (fine needles from acetone).

Phenylpropionic acid peroxide. Melting point 38°.5 (shiny leaflets from diluted alcohol).

Trichloracrylic acid peroxide. Melting point 49° C. (fine leaflets from ethylalcohol).

These peroxides are all as insensible to water as the corresponding anhydrides of the acids.

Inversely it is found that the diacylperoxides, in which the corresponding acid anhydrides are more easily hydrolysed than the acetic acid anhydride, become more and more sensible to water in the same succession.

Acetic acid anhydride hydrates rapidly, the anhydrides of the chlorine substituted acetic acids are more sensible to water according as more chlorine has been substituted. Thus BUCKNEY and THORNSON [1]) say of trichloracetic acid anhydride "der Körper geht bei Anwesenheit der geringsten Spur von Feuchtigkeit in die Säure über".

The analogy to the corresponding diacylperoxides is again great. The acetylperoxide is again completely hydrolysed in aqueous solution within 24 hours (CLOVER and RICHMOND loc. cit.). The monochloracetylperoxide prepared by VANINO and UHLFELDE [2]) is already decomposed when exposed to moist air; while trichloracetylperoxide, which FICHTER [3]) had fruitlessly tried to find, and which we had succeeded in preparing by the application of an artifice, lasts only a few minutes, and when exposed contrivance to air is among others converted to phosgene, probably according to the following reactions;

[1]) Ber. 10, 698, 1877.

[2]) Ber. 33, 1043.

[3]) Helv. 1923, 503.

$$CCl_3COOOCOCCl_3 + HOH \rightarrow CCl_3COOOH + CCl_3COOH$$
$$CCl_3COOOH \rightarrow CO_2 + HCl + COCl_2.$$

The agreement found by us does not only hold for the diacylperoxides of the carbonic acids, but also for those of the sulphonic acids, at least for the only one known, benzene sulphonic acid peroxide.

This peroxide [1]) is very unstable, does not dissolve in cold water, on account of which it can be washed in ice-water, but it gives a separation of iodine in a neutral iodine-iodine potassium solution, as a sign that it is rapidly hydrolysed.

Benzene sulphonic acid anhydride [2]) is likewise insoluble in water, but is very rapidly hydrolysed in aqueous solvents and by moist air.

As it is stated of some substituted sulphonic acid anhydrides, that they are very stable, this might be attributed to their exceedingly small solubility in water. If it should, however, appear that their velocity of hydrolysis is much smaller than that of the non-substituted sulphonic acid anhydride, a corresponding small velocity of reaction is to be expected in the substituted sulphonic acid peroxides.

Delft, May 1925.

[1]) WEINLAND and LEWKOWITZ. Ber. 36, 2702, 1903.
[2]) MEYER and SCHLEGL. Monatshefte **34**, 561, 1913.

Chemistry. — *"Contribution to the Knowledge of the Higher Fatty Acids of Peanut Oil"*. By W. D. COHEN. (Communicated by Prof. BÖESEKEN).

(Communicated at the meeting of May 30, 1925).

Introduction. The constitution of the fatty acids from peanut oil has already repeatedly been studied [1]), and for this reason there would perhaps have been no occasion to return to this subject, if it had not appeared from a publication by EHRENSTEIN and STUEWER [2]) that there still prevails diversity of opinion about the constitution of the higher fatty acids.

Till the appearance of the communication of these last-mentioned investigators it had been considered as proved that the higher fatty acids (i.e. the acids above C-18) from peanut oil consisted of a mixture of arachidic acid, i.e. the normal C-20 acid and the so-called lignoceric acid, i.e. a C-24 acid considered by MEYER and his collaborators — in my opinion on debatable grounds — as an iso-acid, while other investigators (JAMIESON c.s.) do not pronounce an opinion about the structure, but confine themselves to the proof that we have to do here with a C-24 acid. The quantity of each of these two acids would amount to 2—4 % of the total quantity of fatty acids.

Totally discrepant conclusions are arrived at by EHRENSTEIN and STUEWER [2]), who had been struck with the fact that the methyl- and ethyl ester of arachidic acid separated out of peanuts, would not fit into the series of melting points of the esters of palmitic acid, stearic acid, behenic acid, lignoceric acid. The same irregularity would apply to the alcohol made from this arachidic acid with respect to the alcohols C-16, C-18, C-22, and C-24. By means of KOH-melt of erucic acid they prepared the unquestionably "genuine" arachidic acid, which really yielded esters and corresponding alcohols of the expected melting point.

EHRENSTEIN and STUEWER prepared their "arachidic acid" by isolating it from the peanut oil via the methyl ester. In what way this had been done, is not clearly stated. It may, however, be assumed that fractionated

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[1]) SCHWEIZER. Ar. 222, 757 (1884).
MEYER and BEER. Sitz. ber. K. Akad. der Wiss. (Wien) 122, 2B, 567 (1913).
MEYER, BROD, SOYKA. ibid. p. 485 (1912).
HEIDUSCHKA and FELZER. Z. Unt. Nahr. u. Genussm. 38, 241 (1919).
JAMIESON, BAUGHMAN, BRAUNS. Journ. Am. Chem. Soc. 43, 1372 (1921).

[2]) EHRENSTEIN and STUEWER. J. pr. N.F. 105, 199 (1923).

distillation of the esters under reduced pressure has been applied. Now it has been proved with great certainty among others from still unpublished observations in our laboratory that the separation of a natural fatty acid mixture by means of fractionated distillation of the methyl or ethyl esters of the fatty acids with the usual moderate vacuum of the wet air-pump is exceedingly difficult, and that this method practically yields results only for the lower fatty acids (to C-14 inclusive) from cocoanut fat and palmkernel fat. A proper separation of the higher fatty acids is hardly possible[1]), and there is a great chance of getting a constant-boiling mixture of two different esters, which on analysis makes the impression of being a simple substance. EHRENSTEIN and STUEWER have undoubtedly been victims to this misconception, and it is owing to this that they consider the natural arachidic acid as a C-22 acid, not identical with the behenic acid, hence of another configuration.

They have tried to support this conception by a comparison with a synthetic acid, in which it appeared that the melting points corresponded. Particularly with regard to the higher fatty acids, however, the determination of the melting point has comparatively little value, because traces of impurities undetectable by analysis, can considerably affect the melting point, which MEYER has already pointed out. Moreover, the presence of acids with branched chain is very improbable in the natural fats, and the occurrence of iso-acids has, strictly speaking, never been proved as yet with certainty (not by MEYER either for lignoceric acid; this cannot be discussed in detail here).

The investigation described below shows, in my opinion, once more that the fatty acids separated from peanut oil following after stearic acid are C-20 and C-24 acid, C-22 acid being absent, or at most can be present in a quantity so exceedingly small that its presence escapes observation. Of the separated C-20 acid the normal structure has been proved, while the general properties of the C-24 acid render the normal structure the most probable.

I stated above that the usual vacuumdistillation with moderate rarefaction of the air is not adapted to effect an efficient separation for the esters of the higher fatty acids. Fortunately, however, the distillation on extreme vacuum appeared to present an entirely different image, and leads very easily to the end in view, at least in the case in question.

Experimental part. The fatty acids are separated out of 2 kg. of peanut oil, dissolved in 2 litres of 96 % alcohol, and left alone for a long time at about 6°. The crystals that had separated, were sucked off, washed on the funnel with about 200 cm^3 of alcohol, and then twice recrystallized out of the just sufficient quantity of alcohol. Thus were

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[1]) For this reason not much value can be attached to the experimental data of JAMIESON c.s. though there is no doubt that their conclusions are right, and in perfect agreement with mine.

obtained: 80 grammes of fatty acid, melting point 70°, iodine value: 1, average Mol. Weight 337 [1]).

These fatty acids were esterized by boiling for 12 hours with 300 cm^3 abs. ethylalcohol, in which 3 % HCl had been dissolved. On cooling the esters crystallized for the greater part. They were twice remelted with water after sucking off and then twice recrystallized out of little alcohol; they practically contained no free fatty acids any more. Quantity 83 grammes.

The esters were distilled in a simple distillation flask, in which however all the connections were effected by the aid of ground pieces. Between distilling apparatus and pump (make: "Pompe double à Palettes" of Gaiffe-Gallot et Pilon at Paris) there was placed a vessel in a vacuum glass filled with liquid air. With this arrangement a vacuum could be reached and maintained, which always remained under 0,001 mm. Hg.

The distillation (or rather sublimation, for practically no phenomenon of boiling is observed) yielded the following results:

Temp. airbath 210—215°	Quantity	Melting point
Fraction I temp. < 165°	21.5 gr.	41°
„ II „ < 181°	25.0 „	45°
„ III „ < 187° (then the distillation suddenly stopped)	11.0 „	48°
„ IV Residue	24.0 „	52°

It was first tried to determine the saponification values of these fractions; of the higher fatty acids, however, the potassium salts are so strongly hydrolytically split up, that a clear change of colour is not to be observed; for this reason the Mol. Weights of the separated fatty acids were determined by titration in alcoholic solution with alcoholic potassium hydroxyde.

Thus the following values were found:

Mol. Weight acids from fraction I: 315,0
„ „ „ „ „ II: 331,7
„ „ „ „ „ III: 353,8
„ „ „ „ „ IV: 367,8

This so far favourable result was an inducement to continue the fractionated distillation.

[1]) When left for a long time at 0° a good deal still crystallizes out from the collected mother-liquids; part of the crystals were centrifuged off, and dried on filter paper. Melting point 52°. Average mol. w. 274. This is probably a mixture of about equal parts of palmitic acid and stearic acid, which are present in pretty large quantities (compare HEIDUSCHKA loc. cit. and JAMIESON c.s. loc. cit.).

Fraction II and III together distilled again:

	Quantity	Melting point
Fraction Ia boiling point < 165°	11.0 gr.	41°
,, IIa ,, ,, 175°	21.0 ,,	47°
,, IIIa Residue	10.0 ,,	52°

Fraction IIa rectified anew:

	Quantity	Melting point
Fraction Ib boiling point 155°	4.0 gr.	41°
,, IIb ,, ,, < 175°	11.0 ,,	46°
,, IIIb Residue	5.0 ,,	51°

The middle fraction was rectified a few times more (in a smaller and smaller apparatus), thus practically splitting up into two fractions, of which one distilled up to about 155°, melting point 41°, while as residue a substance remained behind with a melting point of 51—52°. Of these two fractions about equal quantities were obtained and combined with the fractions I and Ia etc. resp. with the residues (fractions *A* and B).

The fatty acids were liberated out of both, and then recrystallized many times out of alcohol, at last out of petroleum ether, till the melting points changed no more. At first the C-24 acid showed an entirely different crystalline form, but after it had once been recrystallized with addition of a small quantity of "Norit", the crystalline form characteristic of this series of acids, shiny leaflets, presented itself.

Fraction A gave an acid with the following properties:

glistening crystal leaflets (outwardly perfectly the same as palmitic and stearic acid). Melting point 74.5—75°.

Melting point of the ethyl ester: 42.5°.

Mol. Weight calculated for C-20: 312.3; found 313.1.

C calculated: 76.85 %; found: 76.80 and 76.89 %.

H calculated: 12.90 %; found: 13.01 and 13.10 %.

Through KOH melt of erucic acid I obtained, in excellent yield, an acid with a melting point of 75°, the ethyl ester obtained from it melting at 42.5°. Mixture with the preparations from fraction A did not bring about a change of the melting points. Recently ADAM and DYER [1]) have synthetized arachidic acid by building it up out of stearic acid, they

[1]) ADAM and DYER. Soc. 127, 70. (1925).

found melting point 75—75.5°, melting point of the ethyl ester 42.5°, which is, therefore, in excellent harmony with my values.

Fraction B, shiny crystal leaflets (outwardly not to be distinguished from the preceding acid). Melting point 80—80.5°.

Melting point of the ethyl ester 53.5—54°.

Mol. Weight calculated for C-24: 368.4; found: 367.7.

C calculated: 78.18 %; found: 78.10 and 77.98 %.

H calculated: 13.14 %; found: 13.20 and 13.25 %.

Collecting the values found for the melting points of the two acids and ethyl esters in a table, to which the most probable values are added for palmitic acid, stearic acid, and behenic acid (from the hydrogenated ethyl ester of erucic acid, with the corresponding ethyl ester, we see:

Acid	Melting point acid	Difference	Melting point ethyl ester	Difference
C—16	62.6		24	
		7		9.3
C—18	69.6		33.7	
		4.9		8.8
C—20	74.5		42.5	
		5.0		6.0
C—22	79.5		48.5	
		1.0		5.0
C—24	80.5		53.5	

It is seen from this that the course of the melting points of the homologous acids and the corresponding esters, with the exception of the too low melting point of the C-24 acid, is perfectly regular; the differences in melting point become smaller and smaller when we ascend in the series.

MEYER, BROD, and SOYKA [1]) have built up the normal C-24 acid with the aid of the malonester synthesis from the C-22-iodide. The observation that this acid showed a melting point some degrees higher than the natural acid, renders the conclusion that we should have to do with another isomer, by no means justified. The observation of these investigators themselves on p. 500 of their above cited treatise admonishes to great caution, and makes the value of their melting point diagrams exceedingly dubious [2]).

Now that the normal structure of the C-20 acid has been ascertained, it is for the present the most consistent assumption to assign the normal

[1]) Loc. cit.

[2]) The presence of iso-acids in the natural fats is after all as improbable as the presence of acids with an odd number of carbon atoms. All the communications to this effect, which now and then crop up in the literature, have been refuted with certainty. Compare in this connection the very instructive publication of HEIDUSCHKA and FELZER, which investigators prove that the supposed C-17 acid from peanut oil was nothing but an equimolecular mixture of palmitic acid and stearic acid.

structure also to the C-24 acid from peanut oil. I hope however to return to this point on a future occasion.

Summary.

The higher (saturated) fatty acids from peanut oil contain:

1. *a.* a C-20 acid.
   b. a C-24 acid.
2. the quantity of each of them is 3—4 % of the total quantity of fatty acids.
3. C-22 acid is absent.
4. the C-20 acid is the normal acid and identical with the arachidic acid described so far in the literature.
5. the general properties of the C-24 acid present render it probable that this likewise belongs to the same homologous series of fatty acids.

Delft, May 1925. *Laboratory for Organic Chemistry of the Technical University,*

Physiology. — *"Concerning the supposed Influence of Fructose and the Action of Mg-salts on the Coagulation of Citrate- and Phosphate-blood."* [1]) By Miss E. SLUITER. (Communicated by Prof. G. VAN RIJNBERK).

(Communicated at the meeting of May 30, 1925).

When blood has been made incoagulable by receiving it in a solution of sodium-citrate, it will coagulate after the addition of fructose. The same obtains with citrate-plasma. So for instance

1 cc.	citrate	blood	+	1cc.	fructosesol.	10%	causes	coagulation	after	10 min.
2 „	„	„	+	„	„	„	„	„	„	15 „
3 „	„	„	+	„	„	„	„	„	„	15 „
4 „	„	„	+	„	„	„	„	„	„	15 „
5 „	„	„	+	„	„	„	„	„	„	20 „
6 „	„	„	+	„	„	„	„	„	„	25 „
7 „	„	„	+	„	„	„	„	„	„	25 „
9 „	„	„	+	„	„	„	„	„	„	25 „
1 „	„	„	+	„	1%	did	not	produce	coagulation	

after 45 minutes: but after addition of one more c.c. fructose-solution 1% coagulation appeared after 2 minutes.

My experiments with citrate-plasma yielded the following data:

1 cc.	citrate-plasma		+	1 cc.	fructosesol.	20%	gave	coagulation	after	15 min.
2 „	„		+	„	„	„	„	„	„	15 „
3 „	„		+	„	„	„	„	„	„	15 „
4 „	„		+	„	„	„	„	„	„	30 „
5 „	„		+	„	„	„	„	„	„	100 „
6 „	„		+	„	„	„	„	„	„	4 hrs.

Blood that has been made incoagulable by receiving it in oxalate, Mg sulphate, or by defibrination, does not clot after the addition of fructose [2]). Neither can the phenomenon be evoked by any other sort of sugar, for which I examined glucose, lactose, maltose. and saccharose.

[1]) From experiments in the Laboratory for Physiology at the Amsterdam University.

[2]) Commercial fructose contains traces of calcium: determination by DE WAARD's method made out that 1 cc. 10% fructose contained 0,014 mgrs. Ca; 1 cc. 20% fructose contained 0.027 mgrs. Ca. (the average Ca-content of 1 cc. of bloodserum is 0.1 mgr.). This calcium is not responsible for the coagulation, for when an equivalent quantity of $CaCl_2$-sol., or an equivalent quantity of $CaCl_2$, is added to another sort of sugar, no clotting ensues. Occasionally I also worked with a fructose-solution, to which first a quantity of oxalate, sufficient to bind the calcium had been added, after which the Ca-oxalate had been centrifugalised.

Citrate is one of the few salts that does not precipitate the calcium of the blood, but combines with it in one way or other, a combination thus far only partially known. According to SABBATANI [1]) the anti-clotting action of Na-metaphosphate is due to such a combination. From chemistry we know, in fact, that citrates and alkaline metaphosphates inhibit the precipitation of calcium through the action of oxalates, or render it less complete [2]). This naturally induced us to find out the coagulative action of fructose on phosphatic blood. It thereby appeared that after about half an hour 1 c.c. fructose-solution 20 % produced coagulation in 2 c.c. phosphatic blood or plasma (100 mgrs of metaphosphate to 100 c.c. of blood).

When trying to find an explanation for this phenomenon, I simplified the experimental conditions by making a fibrinogen-solution with which I made the following solutions:

1	fibrinogensol.	in distilled water + fructose	
2	„	in Ringer sol. + citrate + fructose	+ thrombinogen;
3	„	in Ringer sol.	
4	„	in Ringer sol. + citrate	
5	„	in Ca-free Ringer sol. + fructose	
6	„	in Ca-free Ringer sol.	

a few drops of oxalate plasma were added as thrombinogen.

After a short interval clotting ensued in the tubes 2 and 3, while the contents of the other tubes were still liquid after 30 hours. The assumption is warranted, therefore, that the fructose liberates the Ca from the calcium-citrate compound. We know different fructose-calcium compounds; the most probable in this case seemed to be the combination $C_6H_{12}O_6CaO$ or $CH_2OH(CHOH)_3O\begin{matrix}Ca\\ \diamond \\ C\end{matrix}OCH_2OH$, in accordance with the place where oxidation of fructose with HgO + baryta-water occurs.

When adding first a little fructose and then some oxalate to a mixture of $CaCl_2$ + Na-Citrate, or $CaCl_2$ + metaphosphate, which does not give a Ca-reaction with oxalate, a precipitate will be observed after some time, which appears to be calcium. Control solutions were an equal quantity of fructose solution and the Ca-citrate or Ca-phosphate mixture, both with as much oxalate as the Ca-citrate-fructose mixture contained. This, then, seems to show that through the action of fructose on the complex calcium-compound *Ca-ions* have entered into the solution. Some time afterwards I came upon chemically pure, beautifully crystallized fructose (made by KAHLBAUM from inulin). A solution of this preparation did not produce any coagulation, neither in citrate-, nor in phosphate-blood, nor in plasma.

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[1]) Arch. ital. de Biologie T. 39. 1903.

[2]) Vide FRESENIUS. Quantit. Analyse Bd. I. e. 157. 6 Aufl.

There were two possibilities: either the behaviour of fructose prepared from inulin is other than the behaviour of the commercial fructose prepared from saccharose or, besides the Ca, whose quantity had proved to be insufficient for coagulation, the fructose contains still another impurity influencing the clotting.

The plausibility of the first assumption is supported by the researches of KARRER, of IRVINE and of HAWORTH [1]). They derived the methyl-compound from disaccharid, and split it up. This process localized the methylgroup, consequently also the anhydrid compound, as these workers assume that the anhydrid from a disaccharid is the main constituent of a polysaccharid. This method showed HAWORTH that the fructose-residue in the canesugar molecule has another grouping of atoms than the fructose that can be isolated in a permanent form. Now according to IRVINE inulin is derived by polymerization from fructose anhydrid, which as so-called γ-fructose has the same structure as in cane-sugar. So it seems improbable that the permanent product from cane-sugar should be of a different grouping from that derived from inulin. Besides this the rotatory and reducing power of the two kinds of fructose is approximately alike.

As regards the possibility of another contamination of the fructose, e.g. by Ca, I wish to refer to the research by KARPMAN [2]), who studied the effect on coagulation of citrateplasma of a series of organic substances, aliphatic as well as aromatic compounds, of various alkaloids and of some inorganic substances, without being able to demonstrate a clotting action of any of these bodies.

Now, an analysis of the ash of the commercial fructose (the pure fructose left no ash) yielded the singular result that the ash contained, besides an inappreciable quantity of Ca., also $MgCl_2$ in a quantity of 0.64 grms to 100 fructose (as $MgCl_2 + 6$ aq. 1.456 grms). Control-experiments showed that a solution of $MgCl_2$, to this amount really causes coagulation in citrate-blood and phosphate-blood, or-plasma, not however in oxalate-blood. $MgSO_4$ in a solution equivalent to that of $MgCl_2$ has a similar effect. Likewise the experiment with the Ca-Ci-mixture, as described in the experiment with fructose, yielded distinctly a positive result with $MgCl_2$: It appears that Mg liberates Ca from the combination Ca-Ci, which was indicated as such. Of the other alkaline earths Sr gives coagulation in citrate-, and phosphate-plasma, as well as in oxalate-plasma. So its action is similar to that of Ca. This is also borne out by the fact that, from a Sr-Ci mixture, which does not give a precipitate with oxalate, Sr can be expelled by means of $MgCl_2$, a precipitate of Sr-oxalate is obtained. For control-experiment I used a tube with $Sr - Ci +$ water, and a tube with $MgCl_2 +$ water with the amount of oxalate present in the $Sr - Ci + MgCl_2$ mixture. Such an

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[1]) Journ. of the Chem. Soc. (London) 117, 118 (1920) 121, 122 (1922).

[2]) Amer. Journ. of Physiol. 53. (1920).

experiment cannot be carried out with Ba, because the Ba-salt of citric acid is extremely insoluble. The clotting action which I ascribed to the power of fructose to liberate Ca from its complex combination, in the form of ions, appears to be based on a similar action of Mg-salts. This fact might furnish a small contribution to the solution of the problem as to in which form Ca is acting in the coagulation-process, but this paper does not bring forward any evidence regarding the phase in which it happens [1]).

[1]) Concerning the origin of the abnormal quantity of $MgCl_2$ present in the fructose no explanation could be given by the factory of SCHERING at Berlin, where the fructose had been prepared.

Geology. — *"Tertiary Rocks from North-Western British Borneo and from Berau (E. Borneo)"*. By L. RUTTEN.

(Communicated at the meeting of June 27, 1925).

In the last few months I was in a position to investigate a good number of partly fossiliferous tertiary rocks, collected by Dr. W. HOTZ at Basel, and by the late Dr. G. NIETHAMMER in the north-western part of British Borneo, and a larger collection made by Dr. F. WEBER in Berau (E. Borneo). A full description of these collections will be given elsewhere [1]; what follows here are only some results of my investigation.

Rocks from British Borneo.

1. The clastic material occurring in the tertiary rocks is nearly always derived from "old" rocks: the chief component fragments are much worn quartzes and grains of red and green radiolarite, besides much scarcer pieces of slate and intensely weathered fragments of green igneous rocks. Only in two rocks did we find fresh, angular felspars, implying the occurrence of a badly developed tertiary effusive period in this part of Borneo.

2. Tertiary limestones are scarce in British Borneo, however, they occur far into the interior: when we draw a line parallel to the west coast from the G. Kinabolu, which consists chiefly of an acid intrusive rock, we find localities of tertiary limestone to the north as well as to the south of the highest mountain of the island.

3. It is next to certain that the neogene limestones represent only the very oldest part of the Neogene, as is indicated as well by the total absence of Miogypsina as by the regular occurrence of large Lepidocyclinae.

4. In four domains of the Kudat- and Bengkoka peninsula old-neogene and eogene rocks occur intimately bound up with each other: the former with Lepidocyclina, the latter with Orthophragmina.

5. In three rocks from the peninsula of Kudat- and Bengkoka we could recognize distinctly *Orthophragmina in association with Lepidocyclina*, while in three other rocks this occurrence seemed very probable. Inquiries by VERBEEK, MARTIN, DOUVILLÉ, VAN DER VLERK and myself showed that in the Archipelago Orthophragmina rocks representing the Eocene, and Lepidocyclina rocks, representing the Oligocene and the Neogene, are as a rule completely separated, so that up to the present

[1] For Br. N. Borneo see: Verh. Geol. Mijnb. Genootschap Nederl. en Kol. Geol. Serie VIII. 1925, p. 415—428.

nobody ever succeeded in finding the two subgenera of Orbitoides in one and the same rock. Stratigraphically the two genera are, as far as we can see, absolutely separated also in Europa. In America, where, indeed, the development of the tertiary Foraminiferal fauna differs in many respects from that in Europe and Asia, Orthophragmina and Lepidocyclina are found in association in one and the same rock. *Now this contrast is partly done away with by the discovery of Orthophragmina and Lepidocyclina in the same rock in British Borneo.* It might still be imagined that in the rocks of British Borneo perhaps only Lepidocyclina is autochthonous, and that Orthophragmina has been infused from older rocks. This supposition may be dismissed as highly improbable in virtue of various considerations. In the first place such an infusion could be probable only in a region, where a great many older limes occur, and where younger limestones occur in the neighbourhood of older, upheaved limestones. This might still be deemed possible for Kudat peninsula, where limestones are not exactly numerous, but not so very rare either. For the peninsula of Bengkoka, however, where limestones are very rare, such an infusion-hypothesis would require the assumption of too many fortuitous circumstances. Moreover, the assumption of such an infusion might concern one single case, but three occurrences have been demonstrated, and there are probably three more, where Lepidocyclina and Orthophragmina occur together. *We cannot but conclude, therefore, that there are in the Archipelago — though they may be ever so scant — transition strata from Eocene to Oligocene, characterized by the joint-occurrence of Lepidocyclina and Orthophragmina.*

Rocks from Berau. The rocks investigated are derived from North Sangkulirang, from the basin of the Kelai river between Muara Lasan and Tg. Redeb, from the basin of the Lasan river, and from the Sidoöng, Tambalang and Birang, tributary rivers of the Segah or Makam-river. Basing on the literature on Berau, and on the investigation of the rocks we are safe to conclude that tertiary deposits in Berau east of the line Sg. Lasan-Birang-Keburau lama (Bulongan) have a very wide distribution, whereas to the west of that line they are few and far between, and occur probably as relicts. Very likely the tertiary deposits have a thickness of several thousands of meters and can be arranged stratigraphically as follows:

Young Neogene. Limestones with Orbiculina and Alveolinella Boscii in the littoral zone of North-Sangkoelirang near Tg. Domaring; Limestones and lime-sandstones from P. Maratua; brown coal formation of P. Sepinang on the Berau river with carbon containing 30 % water (HOOZE).

Middle Neogene. Coal-sandstone-shale formation of the Lower Kelai- and Makam-rivers with c.a. 14 % water in the pitch-coal (HOOZE), probably occurring also on the Lower Birang (SPAAN), with few fossiliferous banks; on the Kelai river with Miogypsina polymorpha var. spiralis, Lepidocyclina angulosa and Lep. Ferreroi. It may be that limestones and marls of Tg. Domaring, found in the interior, belong to the same level of the Neogene.

Limestones from the Middle Sg. Birang are believed to be somewhat older. They contain beside numerous Miogypsinae (M. aff. Dehaartii) scanty remains of large Lepidocyclinae.

Old Neogene. Limestone formation, characterized by the occurrence of large reef-like limestone hills (Lower Kelai), always with Lepidocyclina formosa, most often with spiroclypoid Heterostegina, with small Lepidocyclina, and numerous other littoral Foraminifera and Corallinaceae. Only once did we find Miogypsina in this formation (Lasan). Widely distributed; Basin Lasan, Lower Kelai, Sg. Sidoöng, and the interior of North Sangkulirang. The limestones belonging to this level, often contain boulders of radiolarite and quartz, potassium felspar, and plagioclase, which must have originated from young, acid tuffs. Rhyolite-, and Dacite-tuffs are perhaps somewhat older than the limestone-formation. Their crystals, as stated above, can often be recognized in the rocks of the lime-formation; they are found in situ in different localities in the basin of Lasan-river.

Young Eogene. Limestones with reticulate Nummulites, Alveolina s. str., Lepidocyclina and large Operculinae occur in the Lasan territory and in the limestone hills to the south of Tg. Redeb (Kg. Lianglangup). There is apparently an intimate sedimentary relation between the old neogene limes, the most recent eogene limestones under consideration, and the somewhat older, but still young eogene limestones, which occur especially on the Upper Lasan, and which are characterized by the absence of Lepidocyclina, and by the frequent occurrence of reticulate Nummulites, Alveolina s. str., large Operculinae and Sorites. Orthophragmina and Assilina are still entirely lacking in these deposits, so that they are to be referred to the young-Eogene.

This stratigraphical table suggests the following remarks. In the first place it strikes us that in North Sangkulirang, in the younger as well as in the older layers of the Neogene, limestones and marls have a wide distribution. We may even call the whole of North Sangkulirang a limestone-marl region, while in the parts of the inland round about Tg. Redeb the Young-, and the Middle-Neogene on the contrary is very poor in limestones, but rich in coal-layers, which seems to show that the facies has become more continental. I think it probable, though not at all a proved fact, that this phenomenon has a similar origin to that of the modifications of the facies in the Tertiary of North-East Kutai, where towards the peninsula of Sangkulirang we note a gradual increase of the marine character of the various sections of the Neogene from W. to E. [1]).

There are a number of facts indicating that in Berau the condition is certainly more complicate than that along the coast of Kutai, where the tectonic of the tertiary littoral hills is always very simple, only poorly folded anticlines being found there, whereas towards the interior the folding becomes intenser, so that eogene deposits in Kutai begin to appear only far into the inland, and the Pre-tertiary still farther. Already at Tg. Mangkalihat eocene limestone occurs very near the coast, [2]) to the south of Sg. Pantei quartzite is known to occur before the coal-bearing Neogene of Tg. Redeb and before the calcareous Neogene of the zone of Lasan-Lower Kelai [3]). MOLENGRAAFF has pointed out that in

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[1]) L. RUTTEN, This Proceedings 1916.

[2]) L. RUTTEN, Samml. Geol. Reichsmus. Leiden. (1) X. 1915. p. 3—10.

[3]) J. A. HOOZE, Jaarb. Mijnw. Ned. Indië. 1886. Techn. Adm. Ged.

some places the mesozoic radiolarites trend eastward from the Lower Sg. Kelai [1]); in the Sg. Galong Ketjil, a tributary of the Lasan river serpentine-breccia and diabase occur eastward from the zone of old-neogene limestones, and lastly also the eogene limestones from the mountain track of Sg. Binai in South Boulongan are located comparatively close to the coast. [2]) It is evident, therefore, that in Berau there are undoubtedly no anticlines that are folded upwards gradually to greater depth, if one is proceeding to the interior. With the altered strike of the mountains — which is still N.N.E. in North Kutai, and becomes N.W. in Berau, as shown clearly by the topographical map, [3]) the geological aspect has apparently entirely changed, the due importance of which cannot be assessed as yet. It is not impossible that the analogues of the less sharply folded littoral anticlines in Kutai are in part lying, in Berau and Bulongan, in the territory covered by the sea. Tarakan and P. Bunju with their oil fields, and incidentally the zone on which P. Maratua is situated, lend support to this view.

In the foregoing we have endeavoured to make up the stratigraphy from the data furnished by the investigation of the Foraminiferal fauna. We feel justified to ask whether we should not exercise special precaution in determining the boundaries on the basis of tertiary Foraminifera, since it becomes more and more evident that there are all sorts of transitions, never thought of before. This will be readily understood if we consider that Lepidocyclina and Orthophragmina have been recognized in British North Borneo in one and the same rock, that remains of Lepidocyclina formosa appear in rocks from Birang territory in typical Miogypsina-deposits, whereas conversely a limestone from the Lasan territory contains remains of Miogypsina together with numerous specimens of Lep.-formosa. It seems to me that the exceptions alluded to imply that the sedimentation in the Malay region — at all events in various localities — has been effected very evenly and uninterruptedly, but that they do not take away from the significance of the Foraminifera with reference to the stratigraphy of the Indian Tertiary. That the stratigraphical schemes produced by VERBEEK-FENNEMA, H. DOUVILLÉ, VAN DER VLERK and the present writer are usable, is indicated by the very fact that the "anomalous fossil-associations" appear as rare exceptions and that in most cases fossil-associations are met with that are in good adjustment with those schemes. As regards the Berau-territory, I think I may therefore be allowed to say that in view of the material examined, it is an established fact that the rocks represented comprise the Young-Eogene up to the Young-Neogene, and that all transitions probably occur within those limits.

It is remarkable that probably old-neogene effusiva occur in the region

[1]) G. MOLENGRAAFF. Verslagen Geol. Sectie Geol. Mijnb. Genootschap I. 1914, p. 175—179.

[2]) L. RUTTEN, Samml. Geol. Reichsmus. Leiden (1). X. 1915. p. 3—10.

[3]) See also P. KRÖKEL, Samml. Geol. Reichsmus. Leiden. (1). X. 1923. p. 141 etc.

under examination, and seem to have a wide distribution there: traces of them were found from Sg. Sidoöng as far as the Upper-Majung over a distance of above 40 km., from the Sg. Sidoöng as far as the interior of Sg. Domaring over a distance of above 100 km. In this connection it is interesting to state that also west of Sangkulirang-Bay rhyolite tuffs have been recognized [1]), though it be in very thin layers. It is moreover possible that the more basic effusiva from Bulongan, as described by KRÖKEL (l. c.), have taken origin in the same period.

In fine I wish to call attention to one thing more. In many tertiary rocks of Berau pebbles or sandy grains of radiolarite have been found. Exactly the same can be stated for numerous tertiary rocks from British North Borneo. Now, from a recent publication by WANNER [2]) we gather that W. HOTZ refers the radiolarites of British North Borneo in part to the Old-tertiary. This induced WANNER to discuss the genesis of the radiolaria-bearing deposits. Concerning this problem the material investigated does not yield conclusive evidence. However, I am inclined to think that the fact that the earliest known fossiliferous tertiary sediments in Borneo invariably contain rounded radiolarite, implies that the folding of radiolaria-bearing rocks must have taken place in the Pretertiary, and that it is not very likely that the radiolarites should still have developed in Borneo in the Tertiary. This can be assumed only if the radiolarian deposits may be considered as sediments in a shallow sea, the upheaval of the seabottom, necessary to bring the radiolarites to the surface, then having been only very inconsiderable, and perhaps only local, so that they could be re-deposited in a rounded condition a little further. If, however, we agree with MOLENGRAAFF and WANNER that the radiolarites are pure deepsea formations, so that they can be deposited again as clastic rocks only after due folding, it will he hard to deny the necessity of assigning to the radiolarites of Borneo a pretertiary age. In that case it is of great interest that according to HOTZ an "ultra-alpine tectonic" must be assumed for British North Borneo.

Utrecht, June 1925.

[1]) L. RUTTEN. These Proceedings, 1916.
[2]) J. WANNER. N. J. f. Miner. Beil. Bd. 45. 1921. p. 149—213.

Geology. — *"Concerning some Erratics of Southern origin in the Dutch Diluvium"*. By J. H. DRUIF. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of June 27, 1925).

In his "Bijdrage tot de kennis der Zuidelijke Zwerfsteenen in Nederland en omgeving" [1]) CH. OOSTINGH reports the occurrence of ferruginous sandstone from the Upper Oligocene and of loose shells from the same formation (resp. p. 101 and 103).

A short time ago on my visit to the railway-cut near Mook I came by chance upon a ferruginous sandstone, which on closer inspection appeared to contain distinctly recognizable cores of Pectunculus obovatus Lamark. On further inquiry I was informed by the stationmaster that a few days previously a fragment of that rock, measuring about $40 \times 20 \times 15$ cm. had been found, and that it contained a good many similar impregnations. But, alas, the workmen, out of curiosity, had knocked it to pieces. The fragment I found was a part of this stone. It is now present in the collection of the Geological Institute of Utrecht. Similar fragments were often found there, as I was told, so that I asked my informant to preserve such finds in future and to communicate with me, which he promised.

On p. 89 of the publication referred to, the occurrence is discussed of the familiar siliceous oolites. To the number of localities mentioned there, I can add one more, viz. "de Stompert" near Amersfoort, where I found a specimen, small but clearly distinguishable, right at the top of the hill. A few days later Mr. R. IJZERMAN brought home more specimens from a visit to the railway-cut at Maarn.

Neither in Dr. OOSTINGH's publication, nor anywhere else to my knowledge, mention is made of an erratic block found in 1884 by LORIÉ near Zeddam, now present in the Utrecht collection. On re-examining that part of the collection, I was struck by a peculiar green mineral enclosed in it.

The rock under consideration is a common white dyke-quartz, coloured yellow here and there, while a grass-green mineral can be recognized, distributed in irregular aggregations, mostly in spots, sometimes more or less spherical, not in distinguishable crystals.

A chemical examination made out that it contained Cu and P, while on treatment with acid initially some CO_2 is emitted. On heating some

[1]) Mededeelingen der Landbouw Hoogeschool. Dl. XIX. Wageningen.

water is given off. It is highly probable, therefore, that we have to do here with one of the minerals from the Lunnite-group [1]).

The habitus is most like Pseudo-Malachite.

The micro-chemical examination confirmed the presence of P.

Now, it is a known fact that in the basin of the Rhine such minerals consisting chiefly of copperphosphate, occur, namely at Ehl near Linz. We may safely conclude, therefore, that the rock originates from that district. Since nothing is known about the occurrence of similar rocks in the basin of the Meuse, we seem to have hit upon a new erratic block characteristic of the Rhine.

[1]) DOELTER: Mineralchemie III, 1, p. 437, 1918.

Palaeontology. — *"A Contribution to the knowledge of the Pleistocene Flora of the Netherlands"*. By F. FLORSCHÜTZ. (Communicated by Prof. L. RUTTEN).

(Communicated at the meeting of June 27, 1925).

In the summer of 1924 a boring was performed for the waterworks of Velp, municipality of Rheden, in the vicinity of the pumpingstation. The bore-hole lies in the domain of the municipality of Rozendaal, 31.30 M. + O. D. (= New Amsterdam Ordnance Datum). On sheet 470 (Rozendaal, edition 1911) of the Government chromotopographical map $\frac{1}{25000}$ it is localized by the eastern intersection of two circles, drawn with radii of 36 and 25 m.m., respectively from the tower of the castle Rosendael and the Rozendaal watercornmill.

The nature of the bored layers was discussed by Dr. J. F. STEENHUIS, geological adviser in the Government Office for the Drinking-water-supply, in a treatise entitled: „Eenige geologische opmerkingen over de in de winplaats der gemeentewaterleiding van Rheden verrichte diepboring, benevens beschrijving der aangeboorde aardlagen" (Some geological observations on the deep-boring in the source of supply of the municipal waterworks of Rheden with a description of the bored layers), which treatise appeared as an annex to the „Rapport inzake de vergrooting van het vermogen der waterwinplaats te Velp" (Report on the raised capacity of the source of water-supply at Velp), made in December 1924 for the municipal corporation of Rheden by the Director of the Office just mentioned.

Down to a depth of 7.80 M. — O. D. the layers consisted of more or less coarse-grained sand, mixed with fine or coarse gravel. Lower down the sand was generally finer, the gravel thinly scattered, while clay- and loamlayers appeared, containing from 28.50 to 28.80 M. — O.D. scales of dark brown peat. In the deepest deposit (85.50 to 90.45 M. — O. D.) Dr. STEENHUIS met with indeterminable shell-fragments, which according to him may indicate that the marine tertiary has been reached. This presumption may be confirmed by the fact that I found in the same layer numerous glauconite-grains and Foraminiferae (especially representatives of the Rotaliidae and of the Nummulinidae).

An examination of the clay revealed that the layer between 23.00 and 28.50 M. — O. D. contained plant-remains, of which I shall give an enumeration lower down as far as I could determine them. Besides the botanical remains I found a couple of fragments of the elytra of a beetle.

My former teacher Dr. ED. EVERTS of the Hague, whom I showed one of these fragments, kindly informed me that it had belonged to a beetle of the genus Donacia.

This fossiliferous layer, 5.50 M. thick, consists, according to the description by Dr. STEENHUIS, of a firm, darkgrey, faintly sandy to plastic, calciferous clay.

The outcome of a further inspection revealed that the clay was mixed with scales of a dark-brown, limeless, fibrous mass, turning black when moistened, and consisting chiefly of fragments of mosses.

The available clay with the fibrous scales was washed and sifted. In the vegetable residue I could demonstrate:

a. Anthophyta: a single or few seeds of Polygonum, Batrachium, Comarum(?), Hippuris, Myriophyllum, Menyanthes, Potamogeton and Carex;

b. Archegoniatae: a large quantity of parts of stems and branches with leaves and single leaves of Musci.

Since the latter appeared to have constituted the chief part of the vegetation, it may not be amiss to look at them more closely.

The first thing that struck me was the predominance of the genus Drepanocladus C. Müll. (syn. Harpidium Sulliv.), identifiable by the falcated tips of the stems and the branches, by the unidirectional leaves, most often curved in a similar way, and by the generally well-developed and differentiated angular cells.

The moss-rests had been so beautifully preserved that all particularities of the leaves, which are of systematic importance (e.g. size and form of the cells, notably of the angular cells), could be observed.

After more than a hundred separate preparations in canadabalsam had been made, the leaves of the stems and the branches being stripped off to increase their transparency, I could reasonably anticipate, in virtue of the marked differentiation of the shape and the size of the leaves, that I should succeed in identifying them with recent Drepanocladi. In fact, the presence of typical species, such as Drepanocladus Sendtneri (Schpr.) Warnst., could readily be established.

On further examination of this genus and the relative literature, however, I resolved for the present to stop my efforts in the determination of the single species, considering that, even if we have entire plants at our disposal, the determination of Drepanocladi entails great difficulties arising from the manyfold morphological varieties. This will readily be understood, if we reflect that the leaves, which are the main criteria in systematization, may vary considerably in one and the same specimen, not only as regards form and dimensions, but also with reference to length and thickness of the nerve, the structure of the cells etc. Outward circumstances seem to be of great influence here.

So long as the students of the systematization of this genus confined themselves to the examination of herbarium-material, the number of

species and varieties increased ad infinitum, until their attention was given to the biological side of the problem. Experience in the study of the ecological factors called for a revision of the adopted system, but did not facilitate a general view of the whole genus. The new idea of collective species may perhaps obviate the difficulties. In face of these facts I think it safer to consider the fossil moss-flora as one whole and to confine myself to deducing a few conclusions from their general characteristics. Among these are in the first place the falcated tips of stems and branches, which seems to be typical of plants emerging partly above the water. Submerged specimens, e.g. of Drepanocladus Kneifii (Schpr.) Warnst. and of Drepanocladus fluitans (L.) Warnst., lack that peculiarity. We may therefore presume with good reason that the mosses had been growing in a shallow bog. The presence of the above-mentioned Anthophyta does not go against that hypothesis.

Another characteristic is the absence of Sphagnaceae. When we correlate this with the lime-content of the clay, it points to what the German plantgeographers call a "Grünlandmoor", in contradistinction to a "Heidemoor", and what in Dutch would be designated by the name of "Laagveenmoeras".

However, peat-formation has apparently not been attained in this case. The pleistocene river soon covered up the plants with silt, subsequently buried them beneath a layer of sand and gravel and clay of about 50 M. thickness, where they remained hidden, until thirsty man disturbed their rest.

Velp (G.) (*Holland*), May 1925.

Physiology. — *"On Cathode-rays as Substitutes of Potassium"*. By Prof. H. ZWAARDEMAKER and T. P. FEENSTRA.

(Communicated at the meeting of June 27, 1925.)

When the heart has been deprived of all the free, diffusible potassium and also of part of the permanent potassium, it comes to a standstill. The pulsations will recommence spontaneously as soon as potassium or any of its radio-active substitutes are administered. This result was achieved with rubidium, thorium, ionium, radium, emanation. Neither the kind of corpuscular radiation, nor its velocity causes any difference in the primary effect. The nature of the effect depends on the inherent physiological disposition of the organ, and further on the dosage, leaving aside a minor adventitious influence of previous condition and accessory circumstances.

Instead of the radio-activity of the radio-active elements added to Ringer's solution we may also apply external radiation. We managed to do this with mesothorium, radium, polonium. In this instance also the kind of radiation did not matter. The effect was the same in all cases examined. The dosis alone was of importance. Too small a dosis proved entirely ineffectual. At a given moment a certain threshold is passed and the effect is achieved. This cannot be attained before a certain latent period is gone through, in which a summation of radiation takes place. A prolonged radiation will again generate a standstill (super-radiation). When the source of radiation is removed an after-effect will be noticed. The speed of the corpuscule is of significance in so far as it determines the amount of radiation that penetrates the pericardium.

In the last few months we have tested the cathode-rays. We procured a cathode-tube with a Lenard window of aluminium, say 9 μ thick. The vacuum we allowed to range between 0,15 and 0,01 mm. Hg., and the current in the secondary circuit of our inductorium between 0,1 tot 0,5 mA. The primary current was drawn from a battery of 8 volts, and the voltage in the spark-gap that was employed as a shunt, may presumably have amounted to 700 volts. The inductorium was of an old construction and not very large, so that we could go on working without the risk of heating the cathode-tube too much. Of course, after some time the aluminium window was burnt through, but it was immediately replaced by a new one. The vacuum was maintained by a rot. Cenco hyvac pump. In the interval between two experiments the amount

of cathode-rays we worked with, was ascertained by roughly estimating their effect upon photographic paper. In the space of ten minutes a distinct blackening was obtained provided that the vacuum was kept lower than 0,03 mm. Hg.

A control experiment proved that a very powerful radiation, such as was used by W. E. PAULI and A. HARTMANN [1]), was completely negative. Not until we remained within the limits stated just now, did we obtain positive results. A current of 0,3 mA. in the secondary circuit and a vacuum of 0.03 mm. Hg. were the conditions we had in view.

At first frogs were the animals we experimented with but when the hot weather suddenly dried up the waters in the province of North-Holland, and fishermen found the frogs dead in their nets, we worked with eel's hearts. The smaller specimens served our purpose better than the larger ones, because with them weaker rays could be taken to penetrate to the nodus atrio-ventricularis.

The frog's heart was attached to a glass Kronecker cannula. After some time the rhythm is noted during 15 minutes' perfusion with normal Ringer's solution. The ligature that held the cannula in its place, was applied as near as possible to the sulcus atrio-ventricularis.

The eel's heart was attached to a simple, straight, glass cannula, held fast by a ligature on the junction between sinus and atrium. Again we waited for regular pulsations during 15 minutes' perfusion with Ringer's solution.

Next we proceeded to Ringer's solution, from which the 100 mgrs of potassium-chloride per liter that it contained at the beginning, had been left out. The water of these fluids had been freshly distilled in glass, and the chemicals had been tested for the absence of potassium (cobalt-nitrite-method). We now looked for the arrest of the cardiac action consequent on the deprival of potassium. Subsequently the organ was suspended at a distance of 6 m.m. from the aluminium window of the cathode-tube, so as to enable the pencil of rays to reach the atrio-ventricular junction in due time.

After a complete standstill of 15 minutes on an average the cathode-radiation was begun and we waited for the pulsations to recommence. If this did not happen within half an hour, the mechanical excitability was ascertained at different intervals. It seemed to us that it was chiefly the powerful rays (the kind that produced in 10 minutes a strong blackening on the photographic paper) that caused inexcitability for mechanical touch.

In a series of experiments with 15 hearts 4 negative cases occurred (the latter only when intense radiation was applied). The eleven positive results are given in the following table.

Even strong hearts cannot stand a long-continued potassium-free per-

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[1]) W. E. PAULI und A. HARTMANN, Arch. f. mikrosk. Anat. Bd. **103**, p. 95, 1924.

TABLE 1.

Revival of the pulsations in a heart that is radiated while it is constantly perfused with potassium-free Ringer's solution.

Data	Animal	Previous standstill (min.)	Latent period until the 1st recovery (min.)	Vacuum m.m. Hg.	Recovery	After-effect	Particulars about the after-effect
8 May	frog	10	20		3 times	no	
20 ,,	,,	10	18		2 ,,	,,	
4 June	eel	48	18	0.08	1 time	yes	
8 ,,	,,	5	17	0.09	1 ,,	,,	in groups
8 ,,	,,	6	3	0.08	1 ,,	no	
9 ,,	,,	30	3	0.08	in groups	,,	
10 ,,	,,	7	15	0.09	1 time	yes	,, ,,
10 ,,	,,	30	3	0.09	1 ,,	,,	
12 ,,	,,	7	25	0.04	1 ,,	no	
13 ,,	,,	7	3	0.02	1 ,,	yes	
15 ,,	,,	5	9	0.02	1 ,,	,,	,, ,,
Average		15	12	0.07			

fusion. It would seem that a prolonged unbalanced condition $\frac{Na + K}{Ca}$ is inconsistent with a lasting automaticity. In order to ensure an indefinite space of time, between the beginning of the standstill and the cathode-radiation, about 50 mgrs. of Caesium-chloride per liter were added. Under the control of Prof. W. E. RINGER this caesium-chloride had been purified of the traces of a radio-active admixture present in the commercial preparation. In two years' time the inactivity of this salt had not changed at all. In 40 minutes the scale of the very sensitive quadrant-electrometer did not shift more than three division marks with 74 grms. of CsCl in a large flat ionization-chamber. So it can be considered to be absolutely inactive, and did not, of itself, make any heart resume its beating when it was added to potassium-free Ringer's solution.

Four hearts were subjected to these experiments. On an average 19 minutes were allowed to elapse between the complete arrest of the heart's action and the commencement of the cathode-radiation. Three hearts gave positive results, one negative. In all probability the radiation had been taken too weak in respect to the size of the heart.

Table II illustrates the positive cases:

TABLE 2.

Recovery of the pulsations in a heart that is radiated while it is constantly perfused with potassium-free Ringer's solution to which is added per liter 50 mgrms of purified, consequently non-radio-active caesium-chloride.

Data	Animal	Previous standstill (min.)	Latent period till 1st recovery	Vacuum mm. Hg.	Recovery	After-effect	Duration of cathode pulsations	After-effect	Particulars about after-effect
16 June	eel	6	10	0.03	in groups	yes	18	249	in groups
18 „	„	20	17	0.02	first continuous	„	195	66	„ „
19 „	„	30	17	0.02	continuous	„	51	150	continuous
Average		19	15	0.02			55	155	

The recovery of the heart-function generally appeared suddenly, without any previous intimation, after a latent period, in which a summation took place of averagely 12 min. in table I and 15 min. in table II.

After some time, however, the restored heart comes to a standstill (super-radiation). Then the cathode-radiation was discontinued and we waited. In half the cases an after-effect revealed itself, which was sometimes of short duration, but at other times could persist even for hours.

The type of recovery is not always the same. In Fig. 1 we have pictured a case of an eel's heart that has been deprived of potassium, and has subsequently been left alone for half an hour. After this long-continued absolute immobility it was exposed to cathode-rays, as above described, while at the same time the permanent potassium-free perfusion was continued. The vacuum measured 0,014 mm. Hg., the secondary current 0,15 mA. During the radiation the vacuum decreased to 0,022 mm. Hg., consequently the secondary current rose to 0,4 mA. After a latent period of 17 minutes, which was attended with a few spontaneous contractions, the latter were resumed very regularly, and gradually at first. These beats continued for 15 minutes. Then the current was interrupted and an after-effect remained, which was originally of a continuous nature, but eventually became grouped.

In Fig. 2 we give another type of recovery. On the left the gradually vanishing pulsations as a result of the deprival of potassium. After waiting 6 minutes the cathode rays were inserted. After 10 minutes the contractions were resumed, and continued, also after cessation of radiation, until far into the night. Meanwhile due care was taken to maintain a perfusion entirely free from potassium.

The penetrating power of the rays differed slightly. In table I the

vacuum averaged 0,08 mm. Hg., in table II 0,02 mm. Hg. We endeavoured to conform the penetrating power of the rays to the size of the heart, but we sometimes failed in our effort.

Fig. 1.

Fig. 2.

In spite of this uncertainty the result was positive in the large majority of cases (14). In the remaining 5 negative cases either the radiation

had been too penetrating and too profuse (3 cases), or the heart was covered by a layer of water (1 case), or the penetrating power was too weak in proportion to the size of the organ (1 case). The latter supposition proved to be true, when in a case that was negative at first, the heart (that had first been restored on normal Ringer's solution) was again brought to a standstill by deprival of potassium, and was finally restored again by a kind of rays of greater penetrating power.

We may, therefore, be justified in concluding that, provided that the circumstances are favourable, also cathode rays are competent to restore the automaticity of a heart that has been brought to a standstill by deprival of potassium.

So besides the mesothorium-, and the radium-rays, the cathode-rays are also to be considered as a physiological agent. The electrons emitted, though they vary as to speed (in the above series their penetrating power decreases $^1/_2$ c., $\frac{1}{2}$ c., $\frac{1}{15}$ c.), carry the same charge (1 unit). On the other hand polonium radiation has a smaller speed ($\frac{1}{20}$ c.) and a positive charge (2 units).

The manner of revival was in every case determined by the organ, not by the stimulant.

For the present we are unable to say to what amount the radiation reaches the nodus atrioventicularis.

EXPLANATION OF THE FIGURES.

Fig. 1. Recovery of the automatic movements by cathode-rays. Vacuum ranged between 0.014—0.022 mm. Hg. in second circuit 0.15 to 0.40 m.A.

Fig. 2. First standstill, then recovery by cathode-rays in the interval between the two white points.

Vacuum ranged between 0.01 and 0.05 mm. Hg.; in second circuit 0.3 m.A. After cessation of the radiation after-effect (continues until far into the night).

Physics. — *"Further experiments with liquid helium. X. On the electric resistance of pure metals, etc. XIV. Influence of elastic deformation on the supraconductivity of tin and indium"*. (Comm. N°. 174 from the Physical Laboratory at Leiden). By G. J. SIZOO and H. KAMERLINGH ONNES.

(Communicated at the meeting of June 27, 1925).

§ 1. *Introduction.*

As no satisfactory theoretical explanation of the supraconductive state of metals has been given yet, which might serve as a guide for further investigations, it seems desirable to try, by changing the external conditions, to discover the factors which play a roll in the appearing of the phenomenon. These considerations led to the institution of an inquiry into the influence which elastic deformation exerts on the appearing of the supraconductive state. The results of this investigation are published here.

In the first place the influence of the elastic extension on the "vanishing-point" was traced with tin, and then that of elastic compression with tin and indium.

A. Extension.

§ 2. *Method of the experiment.*

In the Heliumcryostate [1]) a tinwire (fig. 1. *A*) is placed, stretched vertically between two small tinblocks *B* and *C*. The lower one is kept in place by the glass tube *D*, which is fixed with sealing wax into the cap of the cryostate and the lower brim of which fits exactly in the circular incision in the tinblock. The upper block is carried by a small copper cylinder soldered to the glass tube *E*. This tube is suspended by means of a similar cylinder on the spiral *F*.

The length of the spiral, which is a measure of the applied tension, is read on a millimeter scale placed on the glass tube. In the tube *D* some holes are made so that the liquid may enclose the wire completely. The wire was made (drawn out) from "KAHLBAUM-tin".

The leads necessary for the resistance-measurements are soldered to the tinblocks. Two of them, isolated with glass tubes, pass through holes

[1]) Leiden Comm. N°. 124c (1911) fig. 4.

in the tinblocks (for clearness these tubes are not shown in the figure).

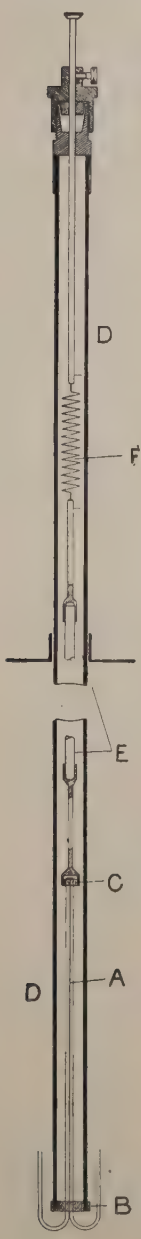

Fig. 1.

The method of resistance-measurements was always that of the balancing of the potential at the ends of the unknown and the known resistance, with the aid of a compensation apparatus of DIESSELHORST, free from thermo-effects. Even below the "vanishing-point" the found potentials were calculated to resistances as if OHM's law held.

The vapour pressures of the heliumbath were read with a cathetometer on a closed mercury manometer. The temperatures were calculated therefrom by aid of the formula of Leiden Comm. N^0. 147*b* (1915) p. 33 [1]).

For this purpose use was made of an accurately constructed curve which represents this formula in the temperature region required.

§ 3. *The measurements.*

The first measurements were made on March 28, 1924. As on the 4th of April following, it was possible to make a more complete series, the results of the first are not communicated here. They were however sufficient for it to be concluded that:

stretching of the tinwire was conducive to the appearing of the supraconductive state.

Namely, we repeatedly ascertained that at a temperature, below that at which the resistance begins to disappear, the resistance of the wire in the stretched was less than in the unstretched state.

On the 4th of April 1924 the measurement was repeated with a new wire of a length of 16.5 cm. and a diameter of 0.30 mm. The resistance of this wire at room-temperature was 0.30 Ω. The results of these measurements are given in table I, and represented by fig. 2.

The resistance-measurements were carried out in the order indicated by the Roman figures. Those indicated by II, III, IV, V, VI form a determination of the "vanishing point" of the unstretched wire; those by VI, VII, VIII, IX, X, XI, XII a similar determination of the stretched wire. The applied tension amounted to 197 grams, i.e. 2.52 k.g./mm^2.

After this the wire was stretched and unstretched alternately, at different temperatures and every time the resistance determined (XIII*b* and XIII*a*, XIV*a* and XIV*b* and *c* XV*b* and XV*a* and *c*).

In the measurement XV the current was maintained through the wire

[1]) See also Leiden Comm. N^0. 167*a* (1923) p. 4, note 1.

TABLE I. Measurements of April 4, 1924.

No.	Tension in G.	Tension in kg./mm².	p_{helium} in mm. Hg.	T	$W_{Sn\text{-}1924\ sp}$
II	0	0	484.9	3.774 K.	0.000181 Ω
III	0	0	473.4	3.753	0.000176
IV	0	0	463.6	3.735	0.000072
V	0	0	453.6	3.716	0.000000
VI	0	0	442.6	3.696	0.000000
VII	179	2.52	442.6	3.696	0.000000
VIII	179	2.52	453.5	3.716	0.000000
IX	179	2.52	463.7	3.735	0.000029
X	179	2.52	467.9	3.743	0.000072
XI	179	2.52	473.3	3.753	0.000165
XII	179	2.52	483.4	3.771	0.000187
XIII^a	179	2.52	477.6	3.760	0.000190
XIII^b	0	0	477.6	3.760	0.000176
XIV^a	0	0	473.7	3.753	0.000183
XIV^b	179	2.52	473.7	3.753	0.000172
XIV^c	207	2.92	473.7	3.753	0.000172
XV^a	207	2.92	468.4	3.744	0.000090
XV^b	0	0	468.4	3.744	0.000133
XV^c	214	3.02	468.4	3.744	0.000086

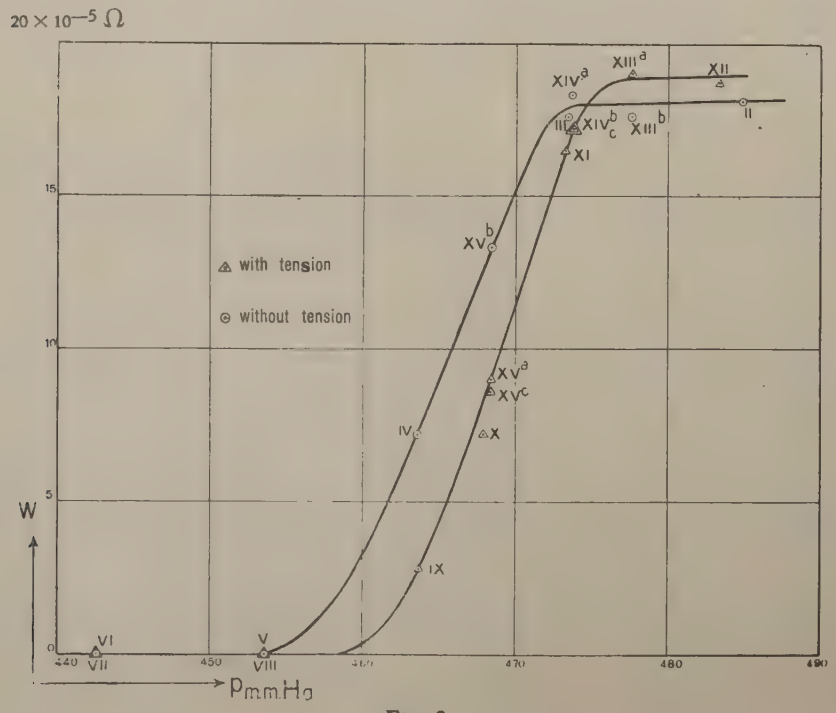

Fig. 2.

during the stretching and unstretching, and the galvanometer was read. It was observed that the latter was displaced about 8 mm., namely during the stretching in the direction corresponding to the diminishing of the resistance, during the unstretching in the opposite direction.

Fig. 2 shows clearly how the "vanishing-curve" is displaced by the stretching of the wire to the side, of the higher temperatures. At the place where the resistance has half disappeared, the displacement amounts to 3.5 mm. Hg., corresponding to 0.007 degrees Kelvin.

In the region of normal conductivity a small increase of the resistanee is to be observed. [1])

During these measurements the electrical current through the wire was always 13 mA. The highest tension with which was measured amounted to 3.02 k.g./mm^2. By trying to increase the tension still a little more, the wire broke. Thus the breaking load had been almost reached.

B. *Compression.*

§ 4. *Method of the experiment.*

The result, stated in § 3, gave rise to the supposition that compression of a tinwire would cause a displacement of the "vanishing-curve" to the side of the lower temperatures. To try this supposition an experiment was planned in which it would be possible to determine the "vanishing-point" of a tinwire, while this was subjected to a hydrostatic pressure. The amount of this pressure would, from the results found with the extension, have to be of the order of 200 kg/cm^2.

The experiment was arranged in the following way:

The resistance to be measured is wound round a small glass tube. The windings are separated from each other by silk thread. Round the resistance coil a second glass tube is slipped. The whole is placed in a copper cylinder (fig. 3. A) [2]), with an inside diameter of 7 mm. and an outside one of 11 mm., closed at the bottom and at the top by a heavy head (screwed and soldered). Two german-silver capillaries pass through the upper. The first one serves for the admission of the helium gas and is connected with the compression apparatus. Through the second the copper wires, necessary for the resistance measurements are led. These wires leave the capillary outside the cryostate by a connecting-piece *D*, in which the packing has been replaced by a little ebonite block. The four little holes, through which the wires are led outside, are afterwards filled up with piceine.

In order to produce the required pressure on the resistance, the cylinder *A*, whilst under the liquid helium, and the leads are first filled from a cylinder with compressed helium to a pressure of about 60 atmospheres.

[1]) See however § 5.

[2]) Compare also Leiden Comm. N^0. 132*b* (1912) fig. 1.

In the cylinder A and in a part of the capillaries liquid helium is formed then. After this, with the aid of a hydraulic press, the pressure is increased to the desired amount. This press is 8 filled with glycerine, which, in two communicating pressureboxes, is separated by mercury from the heliumgas.

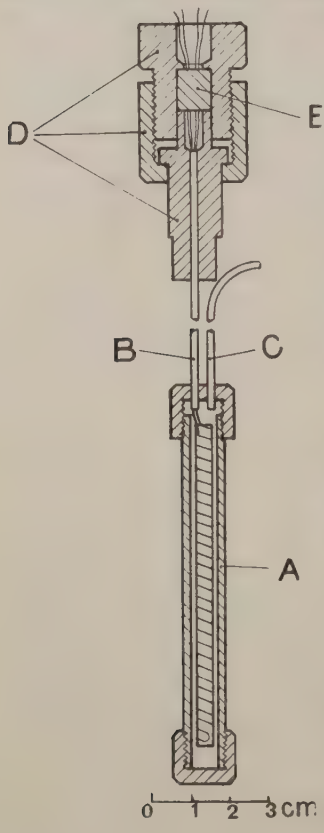

Fig. 3.

For the determination of the pressure two metal-manometers were used with ranges of measurement from 0—150 k.g/cm² and from 0—1500 atmospheres. Both were, after the measurements, calibrated with the small pressure-balance of the Physical Laboratory of Amsterdam. We wish to express our gratitude to Dr. A. MICHELS for his valuable help in this connection.

The resistance-measurements were made in the same way as set out in § 2. Also for the measurements of the vapour pressures and the determination of the temperatures reference may be made to § 2.

§ 5. *The measurements with tin.*

The measurements were made with the resistance Sn-1924-A, wound from a drawn tinwire of diameter 0.24 mm. The material used was "KAHLBAUM-tin". They were carried out on Oct. 24, Oct. 30, and Nov. 14, 1924. On the first two dates they had to be stopped, because of the appearing of a leak in the joint-piece D (fig. 3). A pressure of 300 atmospheres seemed scarcely admissable for the pressure installation, especially for this joint-piece. The last time, however, the measurement could be carried out undisturbed. The current through the wire always amounted to 4 mA.

The results of the measurements are contained in the Tables II, III, IV. They contain determinations of the "vanishing-point" at 4, 95, 193 and 300 kg./cm² hydrostatic pressure. As it was not possible to give all the points in one figure, fig. 4 represents, as an example, the vanishing-curve" at a pressure of 95 kg., whilst in fig. 5 the four curves are given, omitting the measured points. [1])

[1]) In constructing the graphs we always started from the idea that the line representing the disappearance of the resistance ("vanishing-curve") should be a continuous curve. Sometimes, however, by the position of the measured points the suspicion was raised that this supposition was wrong, and that the curve should show one or more discontinuities. To definitely settle down this question, however, a great number of measurements would have to be made and an exceedingly high constancy of the temperature of the heliumbath would be required.

TABLE II. Measurements of October 21, 1924.

Pressure in kg./cm².	p_{helium} in mm. Hg.	T	$W_{Sn.\ 1924\ A}$
4	483.5	3.771° K.	0.00131 Ω
	474.3	3.754	0.00123
	468.4	3.744	0.00077
	464.4	3.736	0.00018
	466.6	3.740	0.00047
	458.5	3.725	0.00000
95	458.6	3.725	0.00000
	464.2	3.736	0.00039
	466.6	3.740	0.00078
	468.5	3.744	0.00097
	474.5	3.754	0.00126
	483.0	3.770	0.00131
	494.0	3.790	0.00131
	466.4	3.740	0.00068
193	474.6	3.754	0.00128
	468.6	3.744	0.00105
	466.5	3.740	0.00092
	464.0	3.735	0.00052

TABLE III. Measurements of October 30, 1924.

Pressure in kg./cm².	p_{helium} in mm. Hg.	T	$W_{Sn.\ 1924\ A}$
4	760	4.2° K.	0.00132 Ω
	493.5	3.788	0.00131
	483.4	3.770	0.00131
	479.4	3.763	0.00130
	479.1	3.763	0.00129
	478.2	3.761	0.00129
	475.8	3.756	0.00126
	473.5	3.753	0.00116
	466.6	3.740	0.00045
	463.4	3.734	0.00008
	460.5	3.729	0.00000
95	494.4	3.790	0.00131
	484.4	3.772	0.00131
	473.7	3.753	0.00126
	468.2	3.743	0.00100
	464.8	3.737	0.00054
	461.0	3.730	0.00008
	458.4	3.724	0.00000

TABLE IV. Measurements of November 14, 1924.

Pressure in kg./cm².	p_{helium} in mm. Hg.	T	$W_{Sn.\,1924\,A}$
4	483.9	3.772° K.	0.00131 Ω
	473.7	3.753	0.00122
	467.8	3.742	0.00071
	463.3	3.734	0.00011
	462.0	3.732	0.00000
300	483.3	3.770	0.00131
	473.2	3.752	0.00127
	469.4	3.745	0.00110
	464.0	3.736	0.00056
	457.1	3.722	0.00000
193	484.5	3.773	0.00131
	473.8	3.753	0.00126
	469.7	3.746	0.00112
	466.4	3.740	0.00089
	463.1	3.734	0.00041
	460.1	3.728	0.00007
95	483.7	3.772	0.00130
	473.7	3.753	0.00126
	469.0	3.744	0.00108
	464.9	3.736	0.00050
	460.6	3.729	0.00007
4	473.9	3.753	0.00122
	468.8	3.740	0.00076
	464.3	3.736	0.00014

The measurements show the correctness of the supposition mentioned in § 4. *The "vanishing-curve" is shifted by the application of the pressure to the side of the lower temperatures.*

The displacement at the place where the resistance has half disappeared, for 300 kg./cm², amounts to 2.4 mm. Hg., corresponding to 0.005 degrees KELVIN. It is noteworthy that the displacement with increasing pressure soon seems to have reached a maximum value. The displacement, corresponding to an increase of the pressure from 193 to 300 kg. is scarcely outside the experimental error.

That the elastic limit is not exceeded by the application of the pressure, is clear from the return of the normal "vanishing-point" when the pressure is released. Also the resistance of the wire at 0° C., which was determined several times before, between, and after the measurements had not changed. It amounted to 2.0199 Ω.

It is noteworthy that in the region of normal conductivity no change

due to the pressure could be observed within the experimental accuracy. This is in agreement with what might be expected from the measurements of KAMERLINGH ONNES en BENGT BECKMANN [1]), who found only a small pressure effect at hydrogen temperatures, which, besides, diminished with temperature. It is understandable that this result has caused some doubts about the reality of the increase of the resistance in the region of normal conductivity found with stretching.

Perhaps this increase, which, besides, is only just outside the experimental error in this region, is to be ascribed to very small fractures in the wire, produced by the stretching.

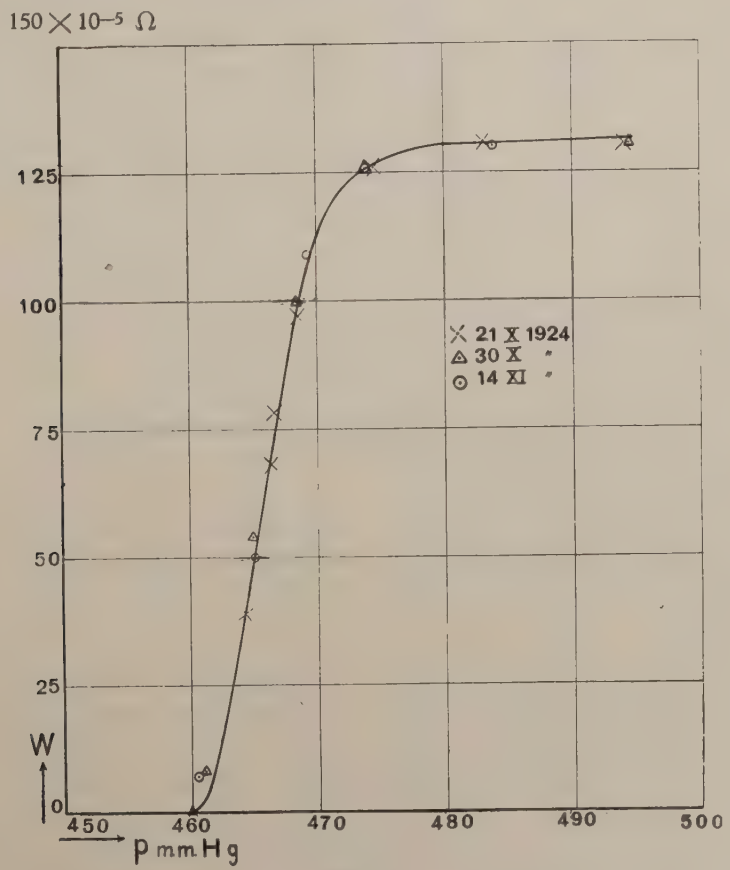

Fig. 4.

§ 6. *The measurements with indium.*

In order to decide the question whether the phenomenon mentioned above is to be regarded as a special property of tin rather than as a general property of the supraconductors, it was considered desirable to repeat the experiment with at least one of the other supraconductive metals. The most suitable for this purpose was indium, as it may be

[1]) Leiden Comm. N⁰. 132*b* (1912).

drawn into wire (in opposition to mercury), as it does not oxidise too fast in the air (in opposition to thallium), whilst besides the situation of the "vanishing-point" is suitable (in opposition to lead).

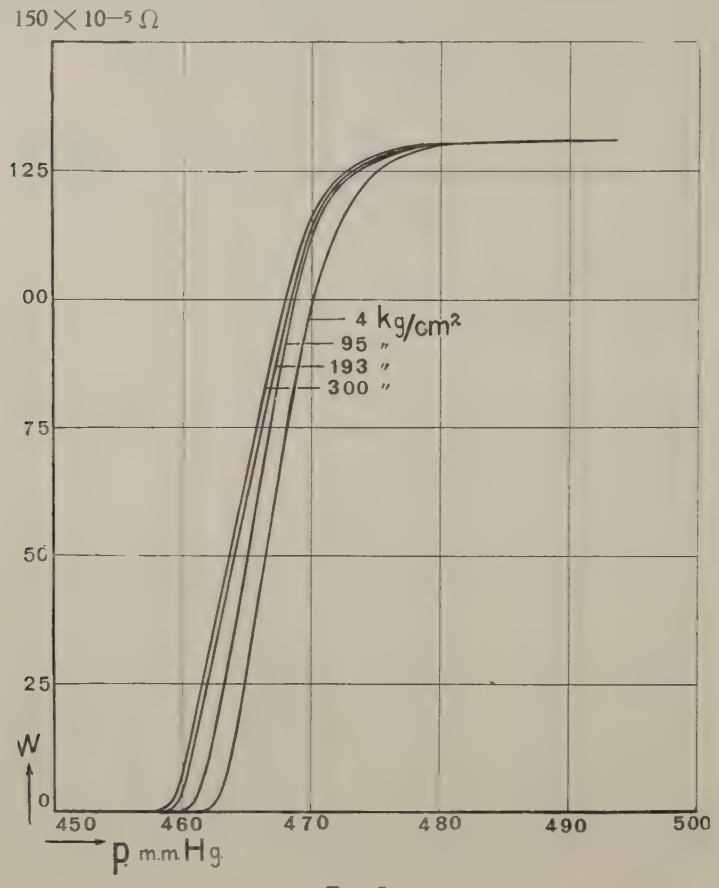

Fig. 5.

The resistance Ind.-1924-A, with which the measurements were carried out, was made of the same wire as that of the resistance Ind.-1922-A, used by W. TUYN [1]). The resistance at 0° C. was 2.2862 Ω.

The measurements were performed in the same way as those with tin. Although the great value of the resistance at the temperatures of liquid helium favoured accurate measurements above the "vanishing-point", it hindered the measurements in the region of the great decrease of resistance; namely, very small temperature changes in the heliumbath cause then very considerable changes in the resistance to be measured. Therefore in this region the measurements were made with a current of only 0.4 mA; above the "vanishing-point" a current of 4 mA. was used. The results follow in the tables V and VI and are represented by fig. 6. The applied tensions were 4,100 and 200 k.g./cm.². respectively.

[1]) Diss. Leiden (1924) p. 29.

TABLE V. Measurements of December 12, 1924.

Pressure in kg./cm².	p_{helium} in mm. Hg.	T	$W_{Ind.\ 1924\ A}$
4	760	4.2° K.	0.07668 Ω
	319.1	3.438	0.07647
	313.5	3.424	0.07647
	308.4	3.412	0.07584
	305.4	3.405	0.0042
	306.6	3.408	0.0338
	306.6	3.408	0.0375
	304.8	3.404	0.0000
100	319.5	3.439	0.07646
	313.2	3.423	0.07646
	308.0	3.411	0.07636
	307.5	3.410	0.07614
	307.8	3.411	0.0757
	305.9	3.406	0.0515
	305.0	3.404	0.022
	305.5	3.405	0.0520
	303.2	3.400	0.0000

TABLE VI. Measurements of December 19, 1924.

Presssure in kg./cm².	p_{helium} in mm. Hg.	T	$W_{Ind.\ 1924\ A}$
200	317.9	3.434° K.	0.07648 Ω
	313.0	3.423	0.07627
	308.1	3.411	0.07608
	306.8	3.409	0.07592
	305.2	3.405	0.0732
	304.8	3.404	0.0643
	304.0	3.402	0.0050
	304.2	3.403	0.0206
	304.5	3.403	0.0284
	304.4	3.403	0.0248
	304.9	3.404	0.0543
	305.5	3.405	0.0704
	305.2	3.405	0.0637
	304.0	3.402	0.0034
	303.2	3.400	0.0000

The results show that the behaviour of indium is the same as that of tin. The displacement of the "vanishing-curve" at the point where the

resistance has half disappeared, for a pressure of 200 kg./cm^2 amounts to 2.1 mm. Hg., corresponding to 0.006 degrees KELVIN, thus only slightly different from that with tin.

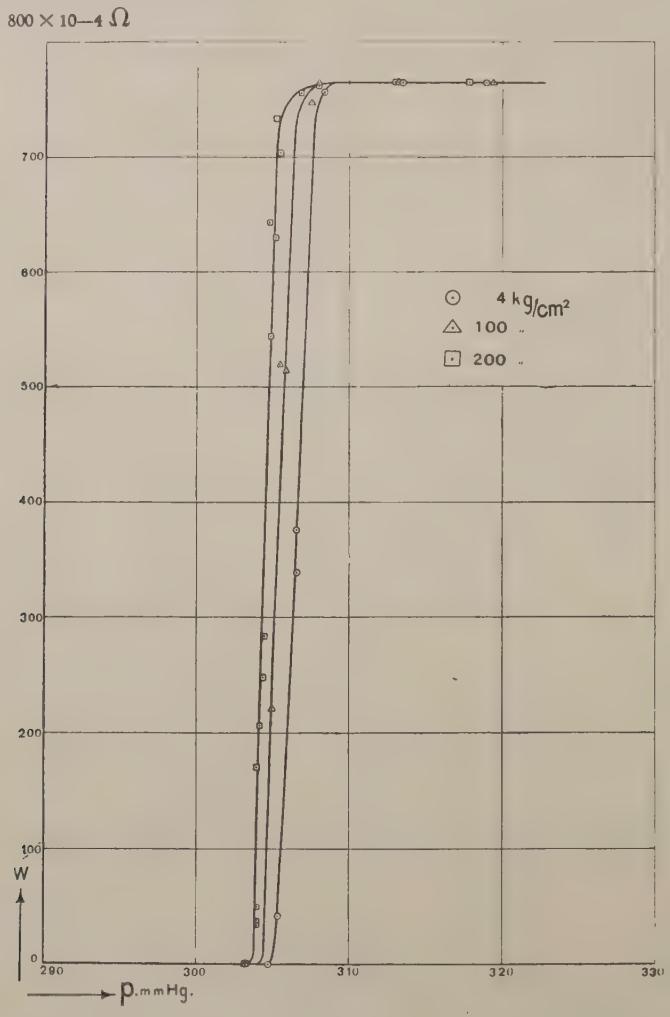

Fig. 6.

§ 7. *Discussion.*

If the extension and the compression of the supraconductive metal may be considered as equivalent to an increase and decrease respectively, of the distances between the atoms, then the results communicated above may be considered as supporting the hypothesis which has been stated in the report of KAMERLINGH ONNES to the IVth Conseil-Solvay, based on the drawings of Dr. H. A. KRAMERS contained therein; namely, that a relatively large space between the atoms is favourable for the appearing of the supraconductive state, when the further special conditions, shown only by the class of supraconductors, are present.

Physics. — "*On the measurement of very low temperatures.* XXXII. *The thermal expansion of Jena-glass, 16^{III}*". By F. P. G. A. J. VAN AGT and H. KAMERLINGH ONNES. (Communication N^0. 176*a* from the Physical Laboratory at Leiden).

(Communicated at the meeting of June 27, 1925).

1. *Introduction.*

Some years ago KAMERLINGH ONNES and HEUSE (Comm. Leiden N^0. 85) and KAMERLINGH ONNES and CLAY (Comm. Leiden N^0. 95*b*) carried out measurements for determining the expansion of Jena-glass 16^{III} in the temperature domain from + 16° tot — 182° C. As data of the behaviour of Jena-glass below this domain were missing, for the volume-determinations at lower temperatures, which were continuously necessary, the above-mentioned results had to be extrapolated to the temperature of liquid hydrogen with the aid of the relative measurements of LINDEMANN [1]) of a rod of an unknown glass, assuming that these measurements would reproduce the character of the linear expansion of glass. As more accurate determinations of the thermal expansion of Jena-glass 16^{III}, of which for example all our gasthermometers are constructed, were necessary, they have been carried out by us to the temperature of liquid hydrogen.

Also, these new measurements are a beginning of a more extensive investigation of the thermal expansion of solid substances at very low temperatures, by which, for example, it should be possible to test the crystal theory of BORN [2]) and the law of DEBYE [3]) from the observations.

2. *Apparatus and method.*

The change of length was measured in the following manner. The inner wall of a vacuum tube, ± 1 M. long, was cooled to the boiling point of ethylene, oxygen, and hydrogen, respectively, the outer wall remaining at room temperature. The movement of the inner wall with regard to the outer wall could be measured accurately by observing, with a microscope, the alterations of position of the platinum points (*C* and *C'*), which were sealed into both the bottom and the top of the

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[1]) CH. L. LINDEMANN. Ueber die Temperaturabhängigkeit des thermischen Ausdehnungscoefficienten. Physik. Z. XII 1911 p. 1197 en XIII 1912 p. 737.

[2]) M. BORN. Zur thermodynamik der Kristallgitter. Z. f. Physik. VII 1921, p. 217, M. BORN, Ueber die Temperaturabhängigkeit der Pyro-electrizität. Physik. Z. XXIII 1922, p. 125.

[3]) DEBYE, Vortrag auf dem Wolfskehl-Kongresz. Göttingen 1913 (B. G. TEUBNER, Leipzig 1913).

inner and outer walls. The observations were made through the plane glass windows (B and B'). The tubes and the microscopes were fixed

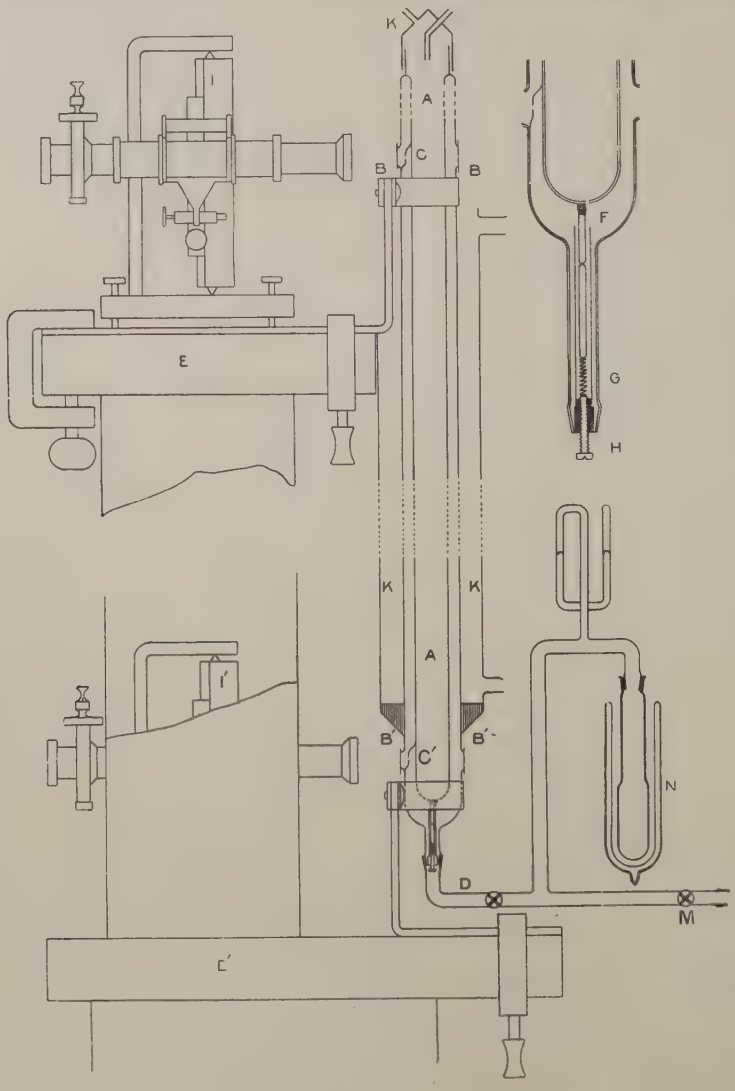


Fig. 1.

rigidly on a stone pillar, a bad conducting, elastic support (F, G) being inserted to prevent oscillations of the long freely hanging inner tube, which would have made measurements impossible. The micrometer eyepieces of the microscopes were calibrated by repeated measurements of some mM. divisions of a standardmeter.

During the measurements the vacuum was maintained by a charcoal tube (N), cooled in liquid air, which as well as the vacuum glass had previously been completely exhausted through the tap M. That part of the outer jacket, which was used for the measurement, was kept at constant temperature by running water.

Before and after each experiment at low temperature one or more measurements were made, with the inner tube kept at room temperature, in order to ascertain whether the tube had returned to its original length.

Before filling the tube with liquid hydrogen, the tube was first cooled by blowing through it for long time hydrogen, cooled with the aid of liquid air. The apparatus could stand this great cooling to 20° K, but the bottom of the inner tube burst at a first measurement at 100° C. by filling the tube with boiling water.

The temperature measurements were made as follows: from the pressure in the gass-reservoir the boiling point at the surface of the bath could be determined. The temperature-difference between the highest and the lowest point could be calculated from the height of the liquid-columns.

Because of the uncertainty of the boiling point of the ethylene it was considered advisable to read the temperature on a gold-resistance-thermometer, which was calibrated with the platinum-thermometer Pt_{23} [1]). Also some measurements were made at $\pm$ 100° C. This temperature was obtained by circulating boiling water, supplied by vacuum pipes, through the inner tube. The temperature was read on a mercury-thermometer, divided in hundredths of degrees.

3. *Results.*

The length of the inner tube, measured between the two platinum points, at 13.1° C., was 893,64 mM. $\pm$ 0.02. By means of a simple calculation the length-difference between inner and outer tubes, both from point to point, could be determined from the measured distances of the points. After having applied some corrections for small temperature-differences we obtain the following results. (See the table on the following page).

From the foregoing the linear expansion of 1 M. of Jena-glass 16^{III} follows:

Temperatures:	Linear expansions:
from 13.1 to 97°.8 C.	0.671 10^{-3} M.
—102.8	—0.770
—182.5	—1.176
—252.8	—1.294

4. *Remarks.*

The accuracy of the micrometer-measurements may be supposed to be about 2 à 3 μ. The results however do not possess this accuracy, as the points did not come back exactly to their original place. Still the differences are but small, as the foregoing tables show.

[1]) The calculations and the temperature-observations for these and following measurements are done by Miss H. v. D. HORST, whom we thank very much for her accurate assistance.

Date	Temp. inside	Temp. outside	$L_{inner}-L_{outer}$	Number of determinations
Measurement in liquid hydrogen.				
6.2.23	13.1	9.1	0.068 mms.	12
6.2.23	— 252.8	9.1	1.226	5
2nd filling	— 252.8	9.1	1.224	5
7.2.23	13.1	9.1	0.073	5
so that the contraction is 1.157 mms. at a temperaturefall from 13°.1 to — 252°.8 C.				
Measurement in liquid oxygen.				
10.2.23	13.1	9.1	0.071	5
10.2.23	— 182.5	9.1	1.132	9
2nd filling	— 182.5	9.1	1.129	9
12.2.23	13.1	9.1	0.089	5
20.2.23	13.1	9.1	0.076	6
20.2.23	— 182.5	9.1	1.126	6
21.2.23	13.1	9.1	0.073	6
so that the contraction is 10.2.23: 1.051 mms. 20.2.23: 1.051 „ at a temperaturefall from 13°.1 to — 182°.5 C.				
Measurement in liquid ethylene.				
27.3.23	14.1	14.1	— 0.081	6
28.3.23	— 102.8	14.1	0.613	15
14.4.23	14.1	14.1	— 0.084	6
from which follows contraction of 0.695 mms. from 14°.1 to — 102°.8 C.				
Measurement at the boiling-point of water.				
30.11.23	13.1	13.1	0.070	10
6.12.23	13.1	13.1	0.053	5
6.12.23	97.8	13.1	— 0.532	10
10.12.23	13.1	13.1	0.076	4
so that a temperature-increase from 13°.1 to 97°.8 C. causes an expansion of 0.599 mms.				

The values obtained for the contraction at ethylene- and oxygen-temperatures are ± 3 and $\pm 6\,^0/_0$ smaller than those, that follow from Comm. No. 95*b* from measurements of the expansion of a rod of Jena-glass 16III. As the measured vacuum tube was already more than ten years old, it was our intention to repeat the measuruments with new Jena-glass in order to observe, how far the age of the glass influences the thermal expansion. Because of lack of time this intention, as well as a measurement with a bath of liquid helium still waits completion.

5. *Representation of the observations by a formula.*

As it appeared to be impossible to represent the results by a third degree equation of the form:

$$l = l_0\left[1 + \left\{a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3\right\}10^{-6}\right]$$

as was the case in Comm. No. 95*b*, and as it was also impossible to obtain another formula with 3 coefficients which would better represent the results, we calculated the coefficients of an equation of the form:

$$l = l_0\left[1 + \left\{a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + d\left(\frac{t}{100}\right)^4\right\}10^{-6}\right]$$

and obtained for them and for the corresponding coefficients of the formula for the cubical expansion the following values:

$a = 716.8$	$k_1 = 2150$
$b = 48.33$	$k_2 = 136$
$c = 9.02$	$k_3 = 27$
$d = 10.9$	$k_4 = 33.$

6. *Graphical representation of the thermal expansion.*

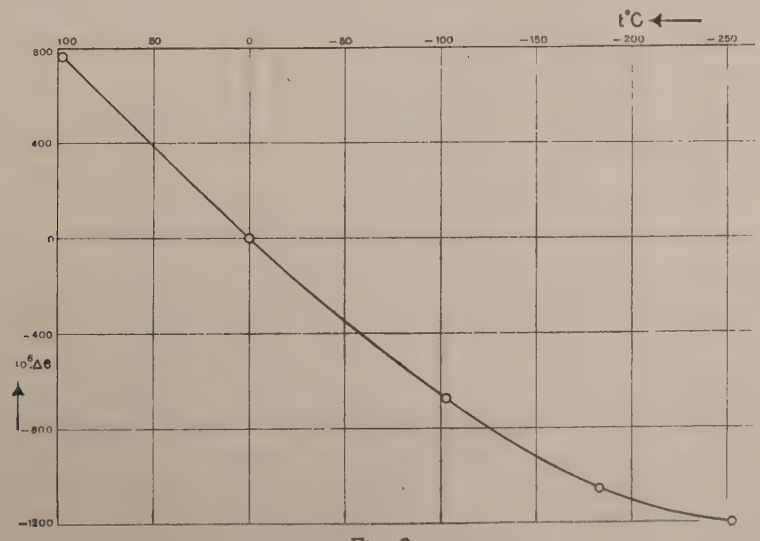


Fig. 2.

With the aid of the foregoing formula the expansion of 1 M. between 13°.1 and 0° C was calculated and after that the length-change from 0° C. downward. Fig. 2 represents the length-change above and below 0° C. and shows, how small this change still is in the hydrogen domain.

7. *The expansion coefficient.*

Though the number of the observations is too small to deduct from them the expansion-coefficient accurately, the general values can still be represented graphically.

We have:

$$\triangle l = l_0 \int_{t_1}^{t_2} a_t \, dt.$$

a_t being the expansion coefficient, $\triangle l$ the length-extension from $t_1°$ to $t_2°$, l_0 the length at 0° C.

Also is

$$\triangle l = l_0 \, \bar{a}_{t_1 t_2} (t_2 - t_1)$$

the mean expansion coefficient between t_1 and t_2 being $\bar{a}_{t_1 t_2}$; and so

$$\int_{t_1}^{t_2} a_t \, dt = \bar{a}_{t_1 t_2} (t_2 - t_1).$$

So the curve, which represents a_t in an a_t, t-diagram, must be drawn so that the left and the right terms of the foregoing equation represent the same areas. So we derive the curve of fig. 3 from the following mean expansion coefficients:

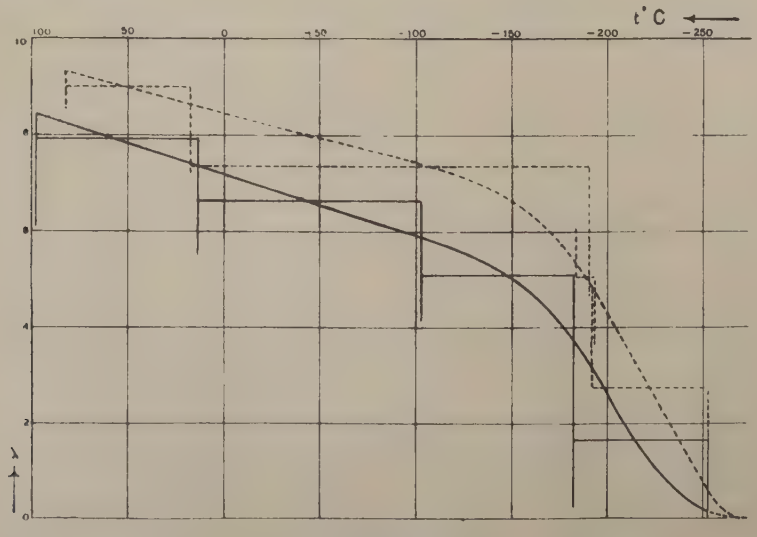


Fig. 3.

$t_2 - t_1$	$10^6\, \bar{\alpha}_{t_1 t_2}$
97.8 — 13.1	7.93
13.1 — (—102.8)	6.64
102.8 — (—182.5)	5.10
182.5 — (—252.8)	1.65.

It is clear that, at low temperature, α_t does not vary linearly with the absolute temperature, but shows the character of the specific heat.

In the last mentioned figure there is also represented the relative expansion coefficient of the unknown kind of glass of LINDEMANN with regard to quartz, derived from his observations. From a comparison with our results it appears, that this curve actually almost represents the character of the glass-expansion. If we suppose that the same is the case for the other substances, of which LINDEMANN has measured the expansion with regard to quartz, we may conclude from fig. 4 in which the

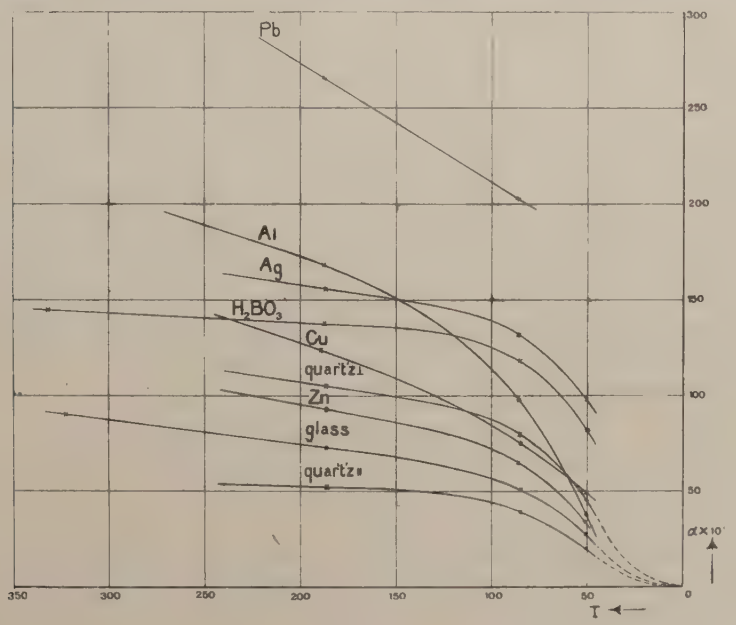


Fig. 4.

expansion coefficient for several solid substances after their results are represented graphically as accurately as possible, that for most substances the form of the curve of the expansion-coefficient is the same as for glass.

Though a further investigation is desirable, our observations, just as those of LINDEMANN, agree better with the law of DEBIJE, after which at sufficiently low temperatures, the expansion-coefficient is proportional to T^3, than with the law of BORN after which at the temperatures in question the expansion-coefficient would be proportional to T.

Physics. — "*Isotherms of mon-atomic substances and their binary mixtures.* XXV. *The same of di-atomic substances.* XXXI. *The compressibility of hydrogen- and helium-gas between* 90° *and* 14° *K.*" By F. P. G. A. J. VAN AGT and H. KAMERLINGH ONNES. (Comm. N°. 176*b* from the Physical Laboratory at Leiden).

(Communicated at the meeting of June 27, 1925).

§ 1. *Introduction.* The investigation of the compressibility of hydrogen- and helium-gas at the boiling-point of hydrogen made by PALACIOS MARTINEZ and KAMERLINGH ONNES (Comm. Leiden N°. 164) has been continued by us particularly at lower temperatures. Also some measurements have been made at the same and at higher temperatures. All the measurements were differential, a method which unexpectedly did not succeed in the first mentioned investigation, as the pressure difference between the hydrogen- and the helium-sides for the high densities appeared to be too great for simultaneous pressure-measurements of both gases. Finally the contents were interchanged in order to investigate if possible asymmetries in the apparatus could influence the results.

The new experiments were especially made for the purpose of determining accurate values for the second virial-coefficient in the empirical equation of state

$$pv = A + Bd + Cd^2 + Dd^4 \text{ etc.}$$ [1])

in order to verify and extend the determinations of the same quantity of KAMERLINGH ONNES and DE HAAS. (Comm. Leiden N°. 127).

In the case of the smaller densities, which were used in our measurements ($d_A \leqq 12$) the influence of the coefficients from C on could be neglected, so that our method was particularly adapted for accurate determination of the B's.

With the B-values obtained it was possible to calculate the corrections for reducing the scales of the international hydrogen- and helium-thermometers to the Avogadroscales of these gases.

§ 2. *The apparatus.*

This was practically the same as that used by PALACIOS MARTINEZ and KAMERLINGH ONNES, discussed in their above-mentioned communication. Only the couplings in the capillaries connecting the pipettes to the thermometer were removed, and the ends of the capillaries soldered

[1]) Comm. Leiden N°. 71.

together. Though this made it somewhat less easy to dismount the apparatus, we decided to do it, after the lead-packing in these couplings, after having kept well closed for some time, began to leak at the most unsuitable moments. The new thermometer T_8 took the place of T_3, which was accidentally broken. Later thermometer T_7 was replaced by T_9 for the measurements below the boiling-point of hydrogen, for, as already mentioned in § 1 PALACIOS MARTINEZ and KAMERLINGH ONNES did not succeed in measuring differentially the third and fourth densities because of the great pressure difference in the thermometers. By replacing one thermometer by a somewhat smaller one of a volume previously accurately calibrated, we succeeded in measuring, differentially, the four densities for hydrogen and helium at the same time.

The volumes of the new thermometers were:

$$T_9 = 103.195 \text{ cM}^3 \qquad T_8 = 110{,}431 \text{ cM}^3.$$

After the whole apparatus had been dismounted, new measurements of the dead space volumes were necessary. For these we obtained:

$$v'_1 = 0.762 \qquad v_1 = 0.772$$
$$v'_m = 0.066 \qquad v_m = 0.067.$$

A thermo-regulator, filled with methyl-chloride, was first used, to maintain a constant temperature in the waterbath containing the pipettes for the pressure determinations at room-temperature. Later the same result was obtained by surrounding the water-bath with a thick mantle of very porous rubber wich did not allow the room-temperature, differing only slightly from the bath-temperature, to change too much. In this way the use of the regulator, generally a difficulty, could be avoided. The following figure represents the result of the method.

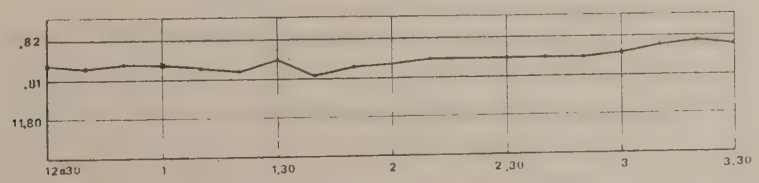


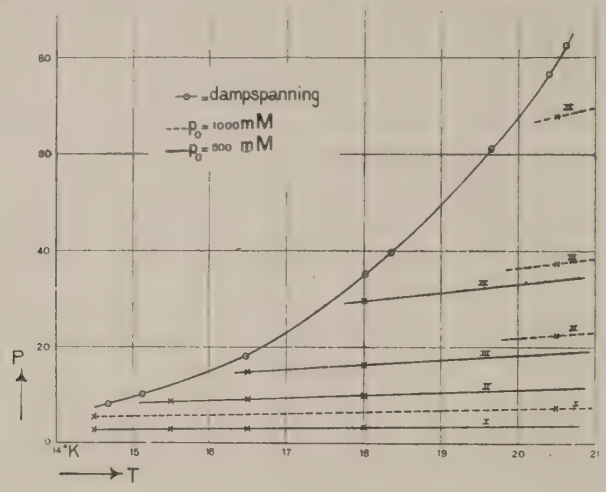
Fig. 1.

§ 3. *Measurements and calculations.*

These were made in the same way as communicated in detail in Comm. N°. 164.

In the case of the determinations at the boiling-point of hydrogen the thermometers and pipettes were filled with ± 1000 mM. hydrogen and helium (zero-pressure) whilst for the measurements below the boiling-point it was necessary to reduce this pressure to about one half in order to avoid condensation of the hydrogen. This made it possible (see fig. 2)

to measure at ± 18° K. with 4, at ± 16,5° K. with 3, at ± 15,°5 K. with 2 densities, and even at 14,°5 K. a measurement with the smallest



dampspanning = vapour tension.
Fig. 2.

density ($d_A = \pm 0.7$) could be made, which could be combined with a determination at about the same temperature with the international hydrogen thermometer, of about twice the density.

Because of the size of the apparatus a smaller zero-pressure was not possible.

Afterwards measurements with the contents interchanged were made with the same zero-pressure and at ± 18° K, so that here also 4 densities could be worked with. The thermometers and pipettes were very carefully exhausted and washed before filling with the new and interchanged gases. The measurements could again be made simultaneously for both sides to the greatest density included.

For the calculation of pressures, virial-coefficients and densities we refer to Comm. N°. 164 (pag. 22).

The following data underlie the calculation of the virial-coefficients at the temperatures of the waterbath.

Hydrogen [1]		Helium [2]	
$A_{A\,0°\,C.}$	0.99942	$A_{A\,0°\,C.}$	0.99970
$B_{A\,0°\,C.}$	0.000580	$B_{A\,0°\,C.}$	0.000512
$A_{A\,100°.20\,C.}$	1.36626	$A_{A\,100°.35\,C.}$	1.36667
$B_{A\,100°.20\,C.}$	0.000863	$B_{A\,100°.35\,C.}$	0.000673

[1]) Comm. Leiden N°. 100*b*.
[2]) Comm. Leiden N°. 102*b*.

From these data and with $\alpha_A = 0.0036618$ the corrections to be applied to the Celsiusscales of the international hydrogen- and helium-thermometer in order to reduce these scale onto the Celsius-Avogadroscales of hydrogen and helium, based upon $\alpha_A = 0.0036618$, could be calculated, by means of the relation

$$\Delta_A = t_{Az} - t_{iz} = \frac{t_{Az} \cdot p_0}{A_{A0°C.} \cdot \alpha_A} \times$$

$$\times \left(\frac{B'_{100}(1+100\alpha_A) - B'_0}{100} - \frac{B'_T(1+\alpha_A t_{Az}) - B'_0}{t_{Az}} \right)$$ [1])

The temperature-determination will be discussed in detail in the following Communication.

§ 4. *Results of the measurements.*

1. *The temperature of the waterbath.* The readings of the mercury-thermometer P. T. R. N°. 46371, corrected after several determinations of its zero-point, were repeatedly controled with the helium- and hydrogen-thermometer. The results were very satisfactory. Some of them are given in the following table.

Mercury-therm.	Helium-therm.	Hydrogen-therm.
15.531	15.540	—
15.527	15.532	—
12.753	12.755	12.752
12.758	12.764	—

2. *The gasquantities.*

Date	Measurements	H_2
23.1.23	in waterjacket	667.91
29.1.23	at 18°,14 K.	—
,,	at 15°,67 K.	—
31.1.23	in waterjacket	667.85
7.2.23	at 90°,23 K.	—
12.2.23	in waterjacket	667.89

[1]) Comm. Leiden Suppl. N°. 23 pag. 904. This equation agrees with Suppl. N°. 51*a* equation (25).

Of another filling:

Date	Measurements	H_2	He
17.6.24	in waterjacket	690.29	741.44
19.6.24	at 69°,85 K.	—	—
21.6.24	in waterjacket	690.33	741.43
24.6.24	at 16°,67 K.	—	—
25.6.24	in waterjacket	690.29	741.44
26.6.24	at 14°,54 K.	—	—
8.7.24	in waterjacket	690.28	741.42

Of the interchanged fillings:

Date	Measurements	H_2	He
17.7.24	in waterjacket	686.30	686.19
18.7.24	at 18°,22 K.	—	—
19.7.24	in waterjacket	686.44	686.32

In this case both gasquantities appear to have increased, from which one might conclude to a small leak at each side. This leak, however, should be just as large for the helium-side as for the hydrogen-side. Hence it seems more probable that for one of the two measurements the temperature has been read incorrectly.

3. Values of pv_A.

a. the left side (movable point-tube) is filled with hydrogen, the right side (stationary point-tube) with helium.

For the sake of completeness the results of PALACIOS MARTINEZ and KAMERLINGH ONNES [1]) at the same temperature, recalculated with the same virial-coefficients at 0° C. and 100° C. and using the same expansion of Jena-glass 16^{III} that unterlies all the present results, must be included here.

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[1]) PALACIOS MARTINEZ and KAMERLINGH ONNES, Comm. Leiden N°. 164.

The results communicated there were calculated for helium with $A_{A0} = 0.99950$ and $B_{A0} = 0.000499$, with the temperature correction for the expansion of glass obtained by extrapolating LINDEMANN's measurements, and so these differ somewhat from those given here.

N°.	Hydrogen			Helium		
	d_A	pv_A	O.—C.	d_A	vp_A	O.—C.
Measurements at 90°,23 K. [1]						
1	0.71898	0.33011	+ 0.00001			
2	2.11256	0.32991	— 3			
3	3.55674	0.32977	+ 1			
Measurements at 69°,86 K.						
1	0.74379	0.25551	+ 0.00003	0.74310	0.25582	+ 0.00003
2	2.19020	0.25518	— 2	2.2150	0.25591	— 3
3	3.68698	0.25487	— 4	3.7153	0.25607	— 2
4	6.64996	0.25436	+ 3	6.6706	0.25641	+ 2
Measurements at 20°,55 K.						
1	1.32349	0.074561	+0.000001	1.32680	0.075229	+0.000037
2	6.42783	0.072163	+ 2	6.68009	0.775170	0
3	8.98884	0.070957	0	9.36906	0.075158	— 1
4	11.4336	0.069804	— 4	11.98147	0.075148	0
Measurements at 20°,53 K.						
1	1.33822	0.074449	—0.000075	1.33583	0.075149	—0.000001
2	3.84188	0.073332	— 5	3.99821	0.075127	— 1
2*				4.00075	0.075137	+ 9
3	6.4228	0.072124	+ 10	6.70706	0.075094	— 8
4	11.5316	0.069687	— 5	12.0625	0.075056	+ 2
4*	11.5322	0.069678	— 14			
Measurements at 20°,51 K. [2]						
1				1.33622	0.075153	+0.000083
2				3.95905	0.075046	+ 0
3				6.62529	0.075024	+ 2
4				11.8983	0.074973	— 1

[1] The helium measurements were discarded as later an impurity was found in the filling.

[2] The hydrogen-thermometer was broken at the beginning of the measurements.

Measurements by PALACIOS MARTINEZ and KAMERLINGH ONNES:

N°.	Hydrogen			Helium		
	d_A	pv_A	O.—C.	d_A	pv_A	O.—C.
	Measurements at 20°,51 K.					
1	1.32857	0.074442	+ 0.000046	1.28965	0.074987	+ 0.000002
2	3.81226	0.073214	+ 5	3.82072	0.074984	+ 18
2*	3.81205	0.073202	— 7	3.82048	0.074945	— 21
3	6.37529	0.071990	+ 6	6.39307	0.074949	+ 2
4	11.4486	0.069555	— 4	11.48163	0.074906	— 3
	Measurements at 20°,49 K. [1])					
1	1.36628	0.074323	— 0.000005			
2	6.43773	0.071937	+ 3			
3	9.00150	0.070728	+ 4			
4	11.4495	0.069566	— 3			
	Measurements at 20°,49 K. [1])					
1	1.31556	0.074350	+ 0.00004			
2	6.37416	0.071930	— 8			
3	8.93236	0.070725	+ 5			
4	11.4188	0.069538	+ 1			

Here follow again the results of our own measurements.

N°.	Hydrogen			Helium		
	d_A	pv_A	O.-C.	d_A	pv_A	O.-C.
	Measurements at 18°,16 K. [2])					
1	0.72114	0.066140	+ 0.000032			
2	2.13567	0.065380	— 5			
3	3.59389	0.064624	— 32			
4	6.48021	0.063202	+ 4			

[1]) On the helium side only the first density was measured.

[2]) See note for the measurements at 90°.23 K. (note 1 p. (679).

N⁰.	Hydrogen			Helium		
	d_A	pv_A	O.—C.	d_A	pv_A	O.—C.
Measurements at 16°,65 K. [1]						
1	0.74516	0.060743	0.000197	0.74442	0.060897	— 0.000045
2	2.20766	0.059776	0	2.23038	0.060905	0
3	3.71491	0.058982	0	3.73868	0.060868	0
Measurements at 15°,64 K. [2]						
1	0.72123	0.056851				
2	1.33022	0.056514				
Measurements at 14°,50 K. [3]						
1	0.74508	0.052630				
2	1.32974	0.052284				
2*	1.32014	0.052297				

b. Interchanged fillings. The left side (movable point-tube) is filled with helium, the right side (stationary-point-tube) with hydrogen. (See table following page).

Before stating the coefficients calculated from these data, for which the corresponding differences between observed and calculated pv_A's are

[1]) If one tries to represent these 3 points by an equation, one finds impossible B-values, and improbable values for O.—C. It seemed better therefore to give little weight to the first density which at these low temperatures is measured with pressures of but a few cm of mercury, and to draw a straight line through the points 2 and 3. The control which would have been given by more points, is lacking in this case.

[2]) At first we found at 15°,67 K.:

1. 0.721228 0.056829.
2. 2.136585 0.055871.

The very large value for B_A which results from these, renders it probable that there is an error in one of the two measurements. Therefore values for d_A and pv_A were calculated from a measurement of CATH and KAMERLINGH ONNES (Comm. Leiden N⁰. 156, table 1*b*) at a somewhat lower temperature, with the differential thermometer filled with helium and hydrogen. Combination of this pv_A with measurement N⁰. 1, both reduced to the same temperature, gives a B_A, which is in complete agreement with all the others, whilst N⁰. 2 does not give that agreement.

[3]) A second point is obtained from the measurements of CATH and KAMERLINGH ONNES mentioned in [2]). Here two determinations could be used, one at a somewhat lower, the other at a somewhat higher temperature.

N°.	Helium			Hydrogen		
	d_A	pv_A	O.—C.	d_A	pv_A	O.—C.
Measurements at 18°,22 K.						
1	0.74063	0.066770	+ 0.000099 [1]	0.74035	0.066294	+ 0.000005
2	2.1940	0.066635	+ 1	2.21855	0.065536	— 7
3	3.6909	0.066599	+ 1	3.71861	0.064787	+ 2
4	6.6472	0.066523	0	6.68772	0.063282	— 4
4*	6.6581	0.066526	— 3			

already given in the foregoing tables, we can make the following remarks:

1. The measurements at 20°,50 K. may certainly (see PALACIOS MARTINEZ and KAMERLINGH ONNES) be supposed to have an accuracy for the pv_A's of $^1/_{10000}$. The same is true for the measurements at 70° and 90° K. For the other measurements, at which the zero-pressure was always 500 mM., this accuracy is reached for the normal-volumes, but not for the pv_A's, as here pressures of 2 à 3 cM. of mercury had to be measured. Moreover once or twice abnormal errors appeared, which are seen in the columns O—C, and which are possibly due to the still too narrow tap-openings, which perhaps were filled up with tap-grease, so that with very small pressure differences there was not a free passage.

2. The accuracy of the B-values is seen best from the complete agreement of the results at 20°,53 K. and 20°,55 K. as well as from the agreement with the B's of PALACIOS MARTINEZ and KAMERLINGH ONNES at these temperatures.

Also at 18°,2 K. the measurements with normal and with the interchanged fillings gave the same values.

With the B-values, derived from only two points, one has to be very careful in drawing conclusions, as appears clearly from the measurement at 15°,6 K., but particularly when the two points are not measured isothermly. The B_A's lying on a smooth curve, (see below) inspire confidence.

The smaller B-values at 70° and 90° K. are proportionally less accurate for the greater values pv_A. The same is true for these of helium at 70° K. and more so for the very small B-values in liquid hydrogen. Still we obtain as the average of three determinations at about the same temperature

$$-0.0000072$$

[1]) This point has been discarded for the calculation of B_A.

whilst PALACIOS MARTINEZ and KAMERLINGH ONNES obtained:

$$-0.0000075.$$

3. After the fillings were interchanged, no deviations, but exactly the same results were obtained, so that there is no reason to suppose any asymmetry.

4. The measurements, including those with interchanged fillings confirm the conclusion, which PALACIOS MARTINEZ and KAMERLINGH ONNES drew, concerning the possible presence of quanta-influences in the form of a term $Qd^{2/3}$ in the equation of state. We also find that the measurements do not necessitate the interpolation of such a term in the equation of state.

5. The B-values of KAMERLINGH ONNES and DE HAAS at 20°,6 and 17°,8 K. differ about 2 and 4 % with those, determined here, whilst the value at 16° K. differs completely.

4. *Virial-coefficients of hydrogen.*

At the measured temperatures following coefficients were obtained:

T	A_A	B_A
90°.23 K	0.33019	— 0.0001202
69.86	0.25562	1939
20.55	0.075182	4700
20.53	0.075158	4740
18.16	0.066472	5053
16.65	0.060938	527
15.64	0.057250	5533
14.50	0.053063	581
interchanged fillings:		
18.22	0.066663	5055
From PALACIOS MARTINEZ and KAMERLINGH ONNES:		
20.51	0.075031	— 0.000478
20.49	0.074973	472
20.49	0.074972	476

Fig. 3 represents the B-values obtained, and also the results of KAMERLINGH ONNES and BRAAK [1]) and of KAMERLINGH ONNES and DE HAAS (resp. indicated by □ and △).

[1]) Comm. Leiden N°. 100a.

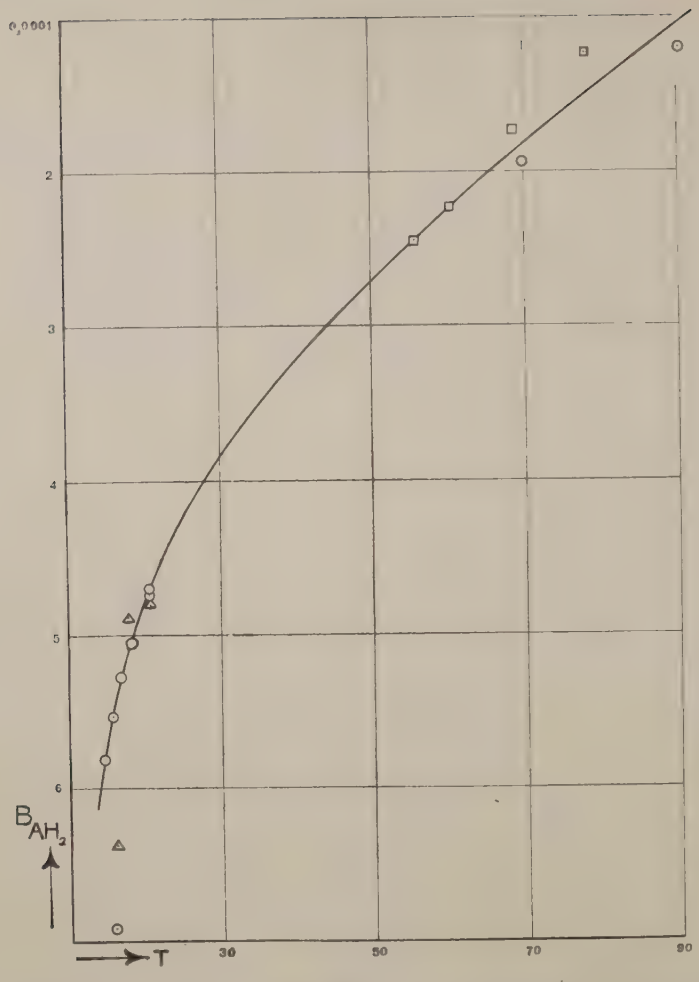


Fig. 3.

From the B-values result the following corrections, to be applied to

Corrections of the international hydrogen-thermometer onto the Celsius-Avogadroscale.

$(\alpha_A - \alpha_{iH_2} = -0{,}000\,0009)$ [1])

T	t	$\Delta_A = t_{A\alpha} - t_{H_2\alpha}$
90.23 K.	— 182.86C	+ 0.067
69.86	203.23	72
20.55	252.54	12 1
20.53	252.56	122
18.16	254.93	131
16.65	256.74	137
15.64	257.45	146
14.50	258.59	155

[1]) The numbers given here are somewhat different from those given in Comm. Leiden Suppl. N°. 51*a* Table XI, owing to the somewhat changed value of $\alpha_A - \alpha_{iH_2}$.

the temperatures on the Celciusscale of the international hydrogen-thermometer, in order to reduce these temperatures onto the Celsius-Avogadroscale of this gas. (Fig. 4).

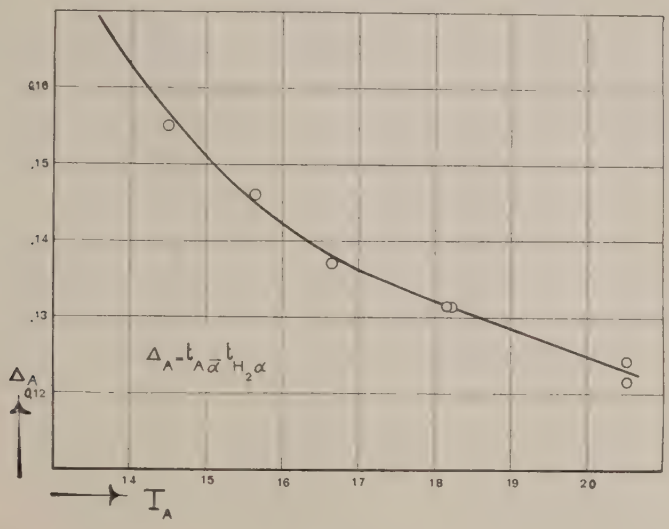


Fig. 4.

5. *Virial-coefficients of helium.*

T	A_A	B_A
69.86	0.25572	+ 0.0001003
20.55	0.075198	— 0.0000042
20.53	0.075162	90
20.51	0.075082	91
18.22	0.066689	244
16.65	0.060960	245
From PALACIOS MARTINEZ and KAMERLINGH ONNES:		
20.51	0.074963	— 0.0000074

We obtain from this graphically the BOYLE-point of helium at 22°,1 K.

From the foregoing results can be calculated the following corrections for the intern. helium-thermometer. (See table following page).

In fig. 5 the results of KAMERLINGH ONNES[1]) are also given, indicated by□.

[1]) Comm. Leiden N°. 102*b*.

Corrections for the international helium-thermometer onto the Celsius-Avogadroscale.

$(\alpha_H - \alpha_{iHe} = 0{,}000\,000\,3^4)$

T	t	$\Delta_A = t_{Az} - t_{Hz}$
69.86 K.	— 203.33C.	+ 0.031
20.55	252.54	41
20.53	252.56	42
20.51	252.58	43
18.22	254.87	46
16.65	256.44	46

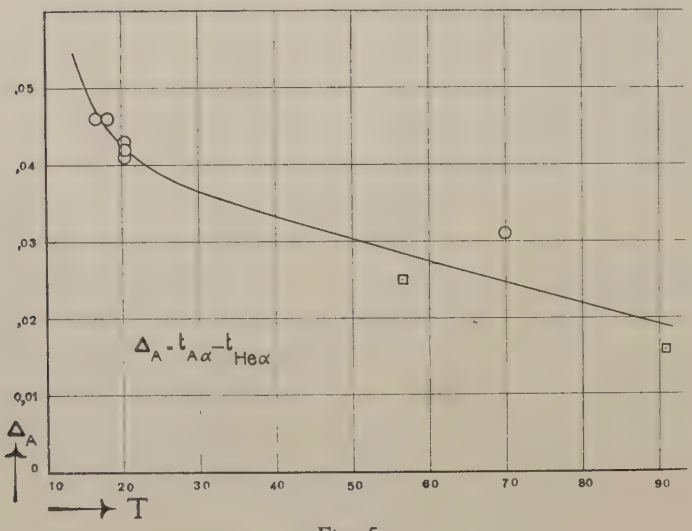


Fig. 5.

Physics. — *"Isotherms of di-atomic substances and their binary mixtures. XXXII. On the behaviour of hydrogen according to the law of corresponding states."* (Comm. N°. 176c from the Physical Laboratory at Leiden). By F. P. G. A. J. VAN AGT. (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of June 27, 1925).

In order to see how far hydrogen deviates from the law of corresponding states the values of B_A and T given in the previous communications are converted into the reduced magnitudes [1]).

The following table is obtained where

$$B' = \frac{B_A}{A_A}$$

$$\mathfrak{B} = \frac{p_k}{RT_k} \cdot B'$$

$$t = \frac{T}{T_k}$$

Hydrogen		
T	t	$\mathfrak{B}$
90.23	2.7194	0.03835
69.86	2.1055	0.07991
20.55	0.6194	0.6586
20.53	0.6187	0.6644
18.22	0.5491	0.7981
18.16	0.5473	0.8008
16.65	0.5018	0.9111
15.64	0.4714	1.018
14.50	0.4371	1.1535
From PALACIOS MARTINEZ and KAMERLINGH ONNES:		
20.51	0.6181	0.6712
20.49	0.6175	0.6633
20.49	0.6175	0.6689

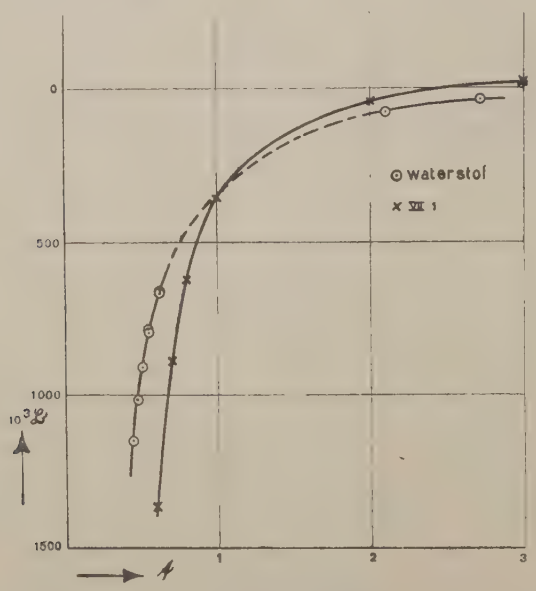
[1]) Comm. Leiden Suppl. N°. 23. Die Zustandsgleichung. Math. Enz. V. 10, p. 116.

In the first place these values can be compared with the values of $\mathfrak{B}$ from the "mean reduced equation of state" of KAMERLINGH ONNES in the form VII 1:

$$10^3\,\mathfrak{B} = 117{,}796 - \frac{228{,}038}{t} - \frac{172{,}891}{t^2} - \frac{72{,}765}{t^4} - \frac{3{,}1788}{t^6}\ ^{1})$$

obtained from the observations:

of AMAGAT for hydrogen, oxygen, nitrogen and ether;
of RAMSAY and YOUNG for ether;
of YOUNG for isopentane.



waterstof = hydrogen
Fig. 1.

It seems valid to consider the $\mathfrak{B}$-values below 20,°50 K. and above 69,°86 K. in fig. 1, as lying on the same curve.

The diagram becomes more remarkable when besides the $\mathfrak{B}$-values of hydrogen, those $\mathfrak{B}$'s are represented, which can be calculated from the B'-values, which CATH and KAMERLINGH ONNES derived from their provisional corrections on the experimental Avogadroscales of hydrogen, oxygen, argon and neon (See table following page).

It then appears from fig. 2, that at temperatures above $t = 1$ the $\mathfrak{B}$-values form a regular series almost corresponding with the increase of the critical temperature. Here again the general rule, given by KAMERLINGH ONNES and KEESOM [2]) is proved, that for substances, for which association is excluded, the critical temperature has an important influence on the whole network of isotherms with regard to the law of corres-

[1]) Comm. Leiden Suppl. N°. 23. p. 117.
[2]) Comm. Leiden Suppl. N° 23. § 34c.

Argon			Nitrogen		
T	t	$10^3\ \mathfrak{A}$	T	t	$10^3\ \mathfrak{B}$
249.04	1.653	— 81.61	241.40	1.916	— 55.90
230.03	1.527	111.4	208.88	1.658	97.29
207.57	1.378	147.9	189.31	1.502	129.2
191.06	1.268	180.1	170.17	1.350	172.8
170.81	1.134	235.8	157.59	1.251	201.1
161.64	1.073	261.9	145.58	1.155	238.9
150.30	0.998	303.7	132.99	1.055	294.8
139.95	0.929	350.6	120.75	0.958	373.9
125.01	0.830	464.6	109.65	0.870	456.7
109.69	0.728	591.6	90.65	0.719	628.0
90.63	0.602	862.2	84.19	0.668	718.8
87.56	0.581	943.1	76.37	0.606	871.2
94.55	0.561	989.2	71.53	0.567	1009.2
81.32	0.540	1056.3	69.57	0.552	1060
Neon			**Oxygen**		
T	t	$10^3\ \mathfrak{A}$	T	t	$10^3\ \mathfrak{A}$
230.15	5.144	+ 59.0	243.51	1.578	— 126.0
208.86	4.668	54.1	214.46	1.390	159.8
185.16	4.145	42.6	180.76	1.171	239.8
170.96	3.821	36.1	170.36	1.104	284.9
157.77	3.526	31.2	157.87	1.023	316.2
145.58	3.254	23.0	145.83	0.945	371.0
133.19	2.977	14.8	133.10	0.863	437.0
120.73	2.698	1.64	120.20	0.779	531.7
90.69	2.027	— 55.8	90.58	0.587	912.2
82.28	1.839	75.5	87.09	0.564	999.1
72.71	1.625	116.6	84.15	0.545	1085.9
64.15	1.434	162.4			
55.91	1.249	224.8			

ponding states. At least for hydrogen, neon, nitrogen and argon this relation exists. Oxygen on the contrary, which for clearness has not

been included in the figure, was almost coinciding with nitrogen. Hence for this substance the rule does not hold. We also see the same difference noted by KEESOM [1]) in a diagram of CATH and KAMERLINGH ONNES [2]) of their vapour pressure determinations.

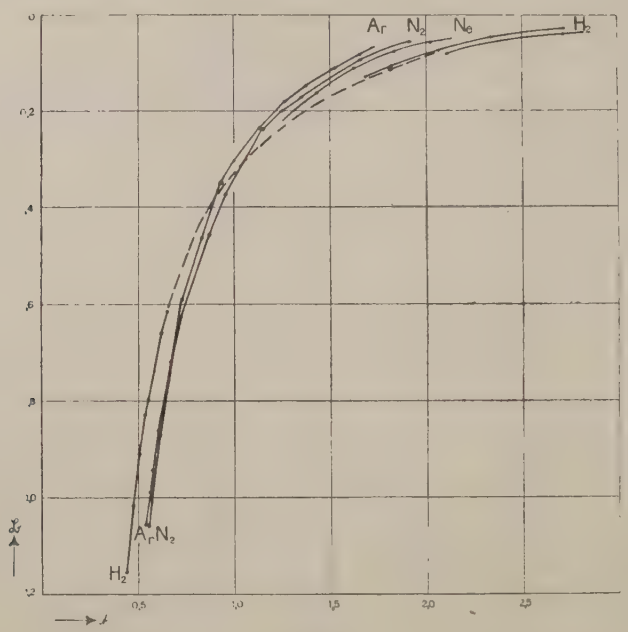


Fig. 3.

It cannot be said how far the method of determination influences the accuracy of the B-values. CATH [3]) has already remarked, that the B'-values of argon determined by him, are generally somewhat greater than those, which result from the measurements of KAMERLINGH ONNES and CROMMELIN.

Also some $\mathfrak{B}$-values of hydrogen, derived from the determinations of KAMERLINGH ONNES and BRAAK are included in the figure; they lie somewhat higher than our values.

On inspecting this diagram the question arises whether, for all this substances, the $\mathfrak{B}$-lines would or would not intersect at about $\tau = 1$. Also in regard to this we regret that the time was too short to determine the B-values of neon below the critical temperature.

Finally we can complete with our B-values the diagram of CATH and KAMERLINGH ONNES [4]), which indicates the changing of $\frac{d(pv)}{dp}$ with the temperature for the same substances.

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[1]) Memorialvolume presented to H. KAMERLINGH ONNES 1922. p. 123.
[2]) Comm. Leiden N°. 152*b*.
[3]) Thesis for the Doctorate, Leiden 1917. p. 77.
[4]) Comm. Leiden N°. 156*a* p. 31.

Here use is made of the relation:

$$\frac{d(\quad)}{d\quad} = \frac{1}{v_k}\frac{d(pv)}{dp} = \frac{B'}{v_k} = K_4 . \mathfrak{B}\ ^1).$$

In this way is obtained:

Hydrogen		
T	$1/t$	$\frac{d(\quad)}{d\quad}$
90.23 K.	0.3677	— 0.12645
69.86	0.4749	0.26349
20.55	1.6146	2.1715
20.53	1.6162	2.1907
18.22	1.8211	2.6314
18.16	1.827	2.640
16.65	1.993	3.004
15.64	2.121	3.358
14.50	2.288	3.803

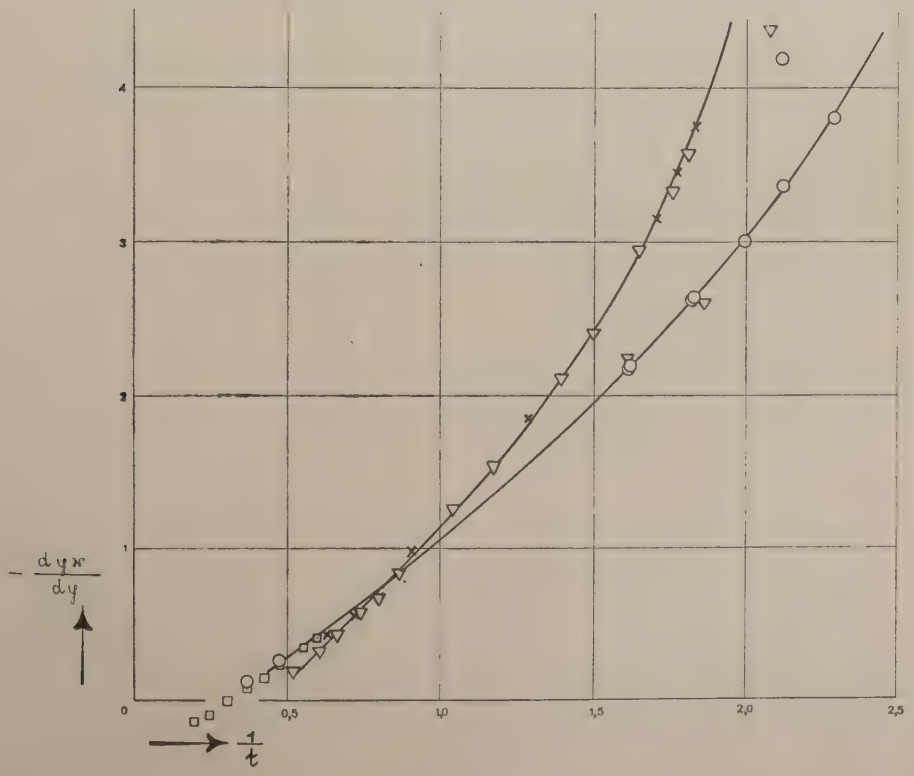

Fig. 3

[1]) Ibid. p. 29.

For reducing the results to reduced magnitudes, use is made of the following data:

	p_k	T_k	v_k
Hydrogen [1]	12.751	33.18	0.002909
Neon [2]	26.86	44.74	
Nitrogen [3]	33.490	125.96	0.004027
Argon [4]	47.996	150.65	0.003357
Oxygen [5]	49.713	154.27	0.003324

[1] Comm. Leiden N°. 151c.
[2] „ „ „ 151*b*. v_k is not known sufficiently.
[3] „ „ „ 145c.
[4] „ „ „ 131*a*.
[5] „ „ „ 117.

Physics. — "*On the measurement of very low temperatures.* XXXIII. *The comparison of the constant volume hydrogen- and helium-thermometers with various zeropoint-pressures.*" (Communication N°. 176*d* from the Leiden Physical Laboratory). By F. P. G. A. J. VAN AGT and H. KAMERLINGH ONNES.

(Communicated at the meeting of June 27, 1925).

1. *Introduction.*

The experiments made with the constant volume differential thermometer, described in the Communication N°. 176*b*, enable us to compare the hydrogen- and helium-scales with each other directly and with very different zeropoint-pressures, for it was possible, using pipettes, to increase considerably the density in the thermometers. The hydrogen- and helium-thermometers were placed side by side at the same height in the low temperature bath, whilst the pressures of both gases were read on the same manometer [1]).

The *B*-values previously mentioned enable the corrections, necessary to reduce the temperatures of the hydrogen- and helium-scales for various zeropoint-pressures onto the Avogadroscales of these gases, to be calculated, so that afterwards the latter could be compared.

During the same time Prof. BEATTIE has carried out in the Leiden Laboratory his research [2]) on the comparison of the hydrogen- and helium-thermometers with various pressures in quartz reservoirs. The fact that the results thereby obtained are not in agreement with those that have been obtained for hydrogen- and helium-thermometers in glass reservoirs certainly raises the importance of both determinations.

2. *The temperatures of the hydrogen- and helium-thermometers on the Celsiusscale.*

If no direct measurements of the zeropoint-pressure had been made, we calculated from the known density (d_A) of the gas in the thermometer at the time of the measurement at the low temperature the pressure which this quantity of gas would exert if it occupied the same volume at 0° C., use being made of the empirical equation of state at 0° C.

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[1]) See further in Comm. Leiden N°. 156.

[2]) Rapport N°. 1 première Commission 4ième Congrès International du Froid. Londen, p. 3.

with the same coefficients that were the basis of the calculation of the quantity of the gas.

The thus found values of p_0 could then be used, together with the directly measured values of the gas pressure in the thermometers at the low temperature (p_t) and with the help of the well known relation

$$t_x = \frac{p_t - p_0}{p_0 \alpha}$$

to calculate the temperatures on the Celsiusscales of the hydrogen- and helium-thermometers [1]). The coefficients of expansion on which these scales are based were calculated in the following way:

CATH and KAMERLINGH ONNES adopted for the coefficients of expansion of the international helium- and hydrogen-thermometers the respective values

$$\alpha_{iHe} = 0.0036614, \text{ resp. } \alpha_{iH_2} = 0.0036627.$$

The provisional international temperaturescale is derived from the scale of the international helium-thermometer, based on 0.0036614 with the help of the provisional correction-table given in Comm. N°. 156*a* table V, col. 2 [2]). An Avogadroscale is thus formed for helium based on 0.0036617[4].

As KEESOM and KAMERLINGH ONNES [3]) remark, the scale of the international hydrogen-thermometer, on the other hand, with the help of the corrections calculated with the *B*-values of KAMERLINGH ONNES and BRAAK, reduces to an Avogadroscale based on 0.0036616[8]. This has the consequence that, extrapolating to $-273°$ C. the Celsius-Avogadroscale for hydrogen should lie 0.003 degrees lower than that for helium (the provisional international scale).

We have preferred to evaluate the Celsius-Avogadroscales for helium and hydrogen on such a basis that, if extrapolating to $-273°$ C., they both give the same value.

For this purpose the expansioncoefficient was calculatcd in each case for a determined zeropoint-pressure from the expression:

$$\alpha = \frac{A_{A0°C} \times 0{,}36618 + (B_{A100°C} - B_{A0°C})\, d_A}{100\,(A_{A0°C} + B_{A0°C} \times d_A)}$$ [4])

which is in agreement with

$$\alpha = 0.0036618 + \left(\frac{B_{100}}{A_0} - 1.36618\frac{B_0}{A_0}\right)\frac{d}{100} - \left(\frac{B_{100}}{A_0} - 1.36618\frac{B_0}{A_0}\right)\frac{B_0}{A_0}\frac{d^2}{100}$$ [5])

where for short

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[1]) Compare the definitions of the temperaturescales in Comm. Leiden Suppl. N°. 51*a*.
[2]) Since reprinted in Suppl. N°. 51*a*, table X*a*.
[3]) Suppl. N°. 51*a*, p. 31.
[4]) Comm. Leiden N°. 101*b*.
[5]) The last term is neglectable except at high densities such as appear here.

$$B_{100} = B_{A100°C}$$
$$B_0 = B_{A0°C}$$
$$A_0 = A_{A0°C}$$
$$d = d_A .$$

The value of $\alpha_A = 0.0036618$ is thus used as a basis, whilst, with the already mentioned values of the virial-coefficients, the following values of the expansioncoefficients for the international helium- and hydrogen-thermometers were obtained

$$\alpha_{i\,He} = 0.0036614^6$$
$$\alpha_{i\,H_2} = 0.0036627^3.$$

The results were still corrected for the small temperature-differences between the different points of a measurement, besides for the first point of some measurements, also for the probable error in the read pressure at the low temperature (p_t), which caused the abnormal deviation (0—C) in the pv_A's, as this error could be calculated from this deviation.

§ 3. *The temperatures on the Celsius-Avogadroscales of hydrogen and helium based on* $\alpha_A = 0.0036618$. (t_{Az}).

The values found could be used to calculate the corrections onto these scales. For this purpose the following expression was used

$$\triangle_A = t_{Az} - t_z = \frac{t_{Az} p_0}{A_{A0°C}\,\alpha_A} \cdot \left[\frac{B'_{100}(1+\alpha_A . 100) - B'_0}{100} - \frac{B'_T(1+\alpha_A t_{Az}) - B'_0}{t_{Az}} \right]^{1)}$$

where $B' = \frac{B_A}{A_A}$

and where for α_A and the virial-coefficients at 0 and 100° C. the already mentioned values were used.

In the following tables (p. 698—700) the so found temperatures and also the corrections for the hydrogen- and helium-thermometers are given. In order to make the results clearer, the temperatures, which all lie below —140° C., have been reduced from the Celsius-Avogadroscales onto the (Kelvin) Avogadroscales of both gases using

$$t_{Az} = T_{Az} - \frac{1}{\alpha_A}\ ^{2)}$$

and these are shown under (T_{Az}).

Finally each isotherm furnishes a direct temperature determination on the Avogadroscale "36618", if they are extrapolated to the density $d_A = 0$, for which condition the equation

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1) Comm. Leiden Suppl. N°. 23 p. 904. This equation is in agreement with Suppl. N°. 51*a* eqn. (25).

2) Comm. Leiden Suppl. N°. 51*a* p. 9.

$$\frac{T_{A\alpha}}{T_{A0°C}} = \frac{A_A}{A_{A0°C}}$$ [1])

still furnishes a value for $T_{A\alpha}$.

§ 4. *Difference in the indication between the Celsiusscales of the helium- and hydrogen-thermometers with different zeropoint-pressures.* (See the tables on the following page).

When the here obtained differences between the helium- and hydrogen-scales were graphed against the zeropoint-pressures (Fig. 1), it was seen that for the same density they increase with decreasing temperature, which is in agreement with earlier measurements.

At the same time it appears that at each temperature they decrease to zero proportionately with the zeropoint-pressure.

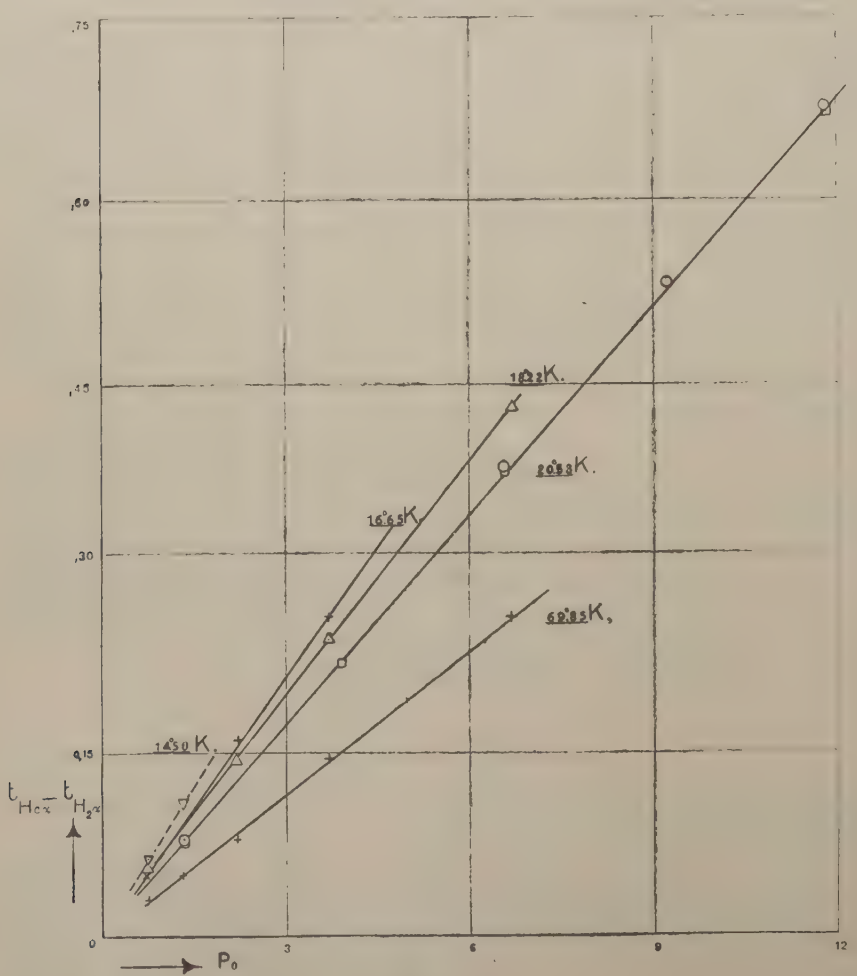

Fig. 1.

[1]) Comm. Leiden Suppl. N°. 51*a* p. 6.

N°.	Hydrogen		Helium		
	p_0	t_α	p_0	t_α	$t_{He\alpha} - t_{H_2\alpha}$
Measurement at 69°,86 K.					
1	0.74369	— 203.272	0.74316	— 203.243	+ 0.029
2	2.19171	203.357	2.21682	203.287	0.073
3	3.69274	203.426	3.72128	203.301	0.129
4	6.67180	203.559	6.69134	203.305	0.254
Measurement at 20°,55 K.					
1	1.32374	— 252.668	1.32730	— 252.589	+ 0.079
2	6.44806	253.134	6.70094	252.751	0.383
3	9.03050	253.367	9.41120	252.835	0.532
4	11.50279	253.589	12.05136	252.913	0.676
Measurement at 20°,53 K.					
1	1.33849	— 252.675	1.33634	— 252.598	+ 0.077
2	3.84811	252.908	4.00520	252.685	0.223
3	6.44297	253.144	6.72808	252.771	0.373
4	11.6020	253.615	12.1334	252.943	0.672
Measurement at 20°,51 K. [1]					
1	1.32882	— 252.709	1.29011	— 252.643	+ 0.066
2	3.81848	252.942	3.82704	252.720	0.222
2*	3.81826	252.945	3.82681	252.729	0.210
3	6.39516	253.182	6.41208	252.802	0.380
4	11.51797	253.647	11.5457	252.964	0.683
Measurement at 18°,22 K. [2]					
1	0.74069	— 254.888	0.740232	— 254.945	+ 0.057
2	2.19580	254.953	2.22011	255.097	0.144
3	3.69676	255.000	3.72452	255.243	0.243
4	6.67883	255.105	6.70978	255.536	0.431
4*	6.67879	255.104			
Measurement at 16°,65 K.					
1	0.74505	— 256.517	0.74448	— 256.474	+ 0.043
2	2.2092	256.663	2.2322	256.500	0.163
3	3.7209	256.816	3.7448	256.562	0.254
Measurement at 14°,50 K.					
1	0.74497	— 258.676	0.74452	— 258.612	+ 0.064
2 [3]	1.3156	258.546	1.3181	258.442	0.104
2* [3]	1.3177	259.085	1.3189	258.974	0.111

[1] From PALACIOS MARTINEZ and KAMERLINGH ONNES. [2] Different filling.
[3] Calculated from CATH and KAMERLINGH ONNES, Comm. Leiden N°. 156.

§ 5. *Temperature-measurements on the Avogadroscale of hydrogen and helium based on* $\alpha_A = 0.0036618$.

N°.	Hydrogen			Helium		
	p_0	Δ_A [1]	$T_{A\alpha}$	p_0	Δ_A	$T_{A\alpha}$
Measurement at 90°, 23 K.						
1	0.71886	+ 0.036	90.232			
2	2.11393	0.106	90.226			
3	3.56201	0.179	90.217			
	extrapolating to $d_A = 0$:		90.221			
Measurement at 69°,86 K.						
1	0.74369	+ 0.040	69.859	0.74316	+ 0.018	69.864
2	2.19171	0.117	69.842	2.21682	0.054	69.849
3	3.69274	0.201	69.841	3.72128	0.090	59.855
4	6.67180	0.363	69.858	6.69134	0.159	69.890
	extrapolating to $d_A = 0$:		69.848			68.855
Measurement at 20°,55 K.						
1	1.32374	+ 0.122	20.544	1.32730	+ 0.041	20.542
2	6.44806	0.592	20.548	6.70094	0.207	20.546
3	9.03050	0.829	20.552	9.41120	0.290	20.545
4	11.50279	1.056	20.557	12.05136	0.372	20.549
	extrapolating to $d_A = 0$:		20.538			20.542
Measurement at 20°,53 K.						
1	1.33849	+ 0.128	20.540	1.33634	+ 0.043	20.535
2	3.84811	0.359	20.541	4.00520	0.125	20.530
3	6.44297	0.600	20.546	6.72808	0.208	20.527
4	11.6020	1.081	20.550	12.1334	0.374	20.521
	extrapolating to $d_A = 0$:		20.536			20.532
Measurement at 20 ,51 K.						
				1.33673	+ 0.043	20.515
				3.96589	0.127	20.511
				6.64578	0.213	20.511
				11.96723	0.382	20.528
				extrapolating to $d_A = 0$:		20.510

[1] In all these tables Δ_A signifies : $t_{A\alpha} - t_{He\alpha}$ for helium.
and $t_{A\alpha} - t_{H_2\alpha}$ for hydrogen.

No.	Hydrogen			Helium		
	p_0	Δ_A	$T_{A\alpha}$	p_0	Δ_A	$T_{A\alpha}$
Measurement at 20°,51 K. [1]						
1	1.32882	+ 0.125	20.506	1.29011	+ 0.041	20.488
2	3.81848	0.358	20.506	3.82704	0.122	20.492
2*	3.81826	0.358	20.503	3.82681	0.122	20.483
3	6.39516	0.600	20.508	6.41208	0.204	20.492
4	11.51797	1.081	20.524	11.5457	0.367	20.493
	extrapolating to $d_A = 0$:		20 502			20.488
Measurement at 20°,49 K. [1]						
1	1.36657	+ 0.125	20.483			
2	6.45804	0.593	20.492			
3	9.04328	0.830	20.495			
4	11.51885	1.057	20.498			
	extrapolating to $d_A = 0$:		20.487			
Measurement at 20°,49 K. [1]						
1	1.31581	+ 0.123	20.493			
2	6.39403	0.595	20.487			
3	8.97346	0.836	20.491			
4	11.4878	1.070	20.491			
	extrapolating to $d_A = 0$:		20.486			
Measurement at 18°,16 K.						
1	0.721025	+ 0.070	18.164			
2	2.13708	0.213	18.164			
3	3.59932	0.359	18.154			
4	6.50035	0.646	18.166			
	extrapolating to $d_A = 0$:		18.163			
Measurement at 16°,65 K.						
1	0.74505	+ 0.078	16.651	0.74448	+ 0.024	16.650
2	2.2092	0.231	16.658	2.2322	0.071	16.661
3	3.7209	0.380	16.654	3.7448	0.119	16.648
	extrapolating to $d_A = 0$:		16.651			16.643

[1] From PALACIOS MARTINEZ and KAMERLINGH ONNES.

N°.	Hydrogen			Helium		
	p_0	Δ_A	$T_{A\alpha}$	p_0	Δ_A	$T_{A\alpha}$
Measurement at 14°,50 K.						
1	0.74496	+ 0.088	14.502	0.74452	+ 0.026	14.504
Measurement at 18°,22 K. (different filling)						
1	0.74023	+ 0.074	18.219	0.74069	+ 0.027	18.229
2	2.22011	0.222	18.215	2.19580	0.078	18.215
3	3.72452	0.372	18.219	3.69676	0.130	18.220
4	6.70978	0.671	18.225	6.66783	0.236	18.221
4*				6.67879	0.236	18.222
extrapolating to $d_A = 0$:			18.215			18.218

The method of temperature-measurement followed here thus gives practically the same temperature results, even with very divergent zero-point-pressures and even with densities many times the density of the international gas-thermometers, where the corrections of the Avogadro-scale exceed one degree (for hydrogen). This is true for each gas individually, as well as for the comparison of the two gases.

If only those measurements are considered which have a zeropoint-pressure of 1000 mM., or where these are lacking those with densities lying immediately above and below it, then only the following differences remain between these experimental Avogadroscales of hydrogen and helium:

T	p_0	$T_{A\alpha He} - T_{A\alpha H_2}$
69.86	± 0.74	+ 0.005
	2.19	+
20.55	1.32	— 2
20.53	1.34	— 5
18.22	0.74	— 10
	2.21	0
16.65	0.74	— 1
	2.23	+ 3
14.50	0.74	+ 2